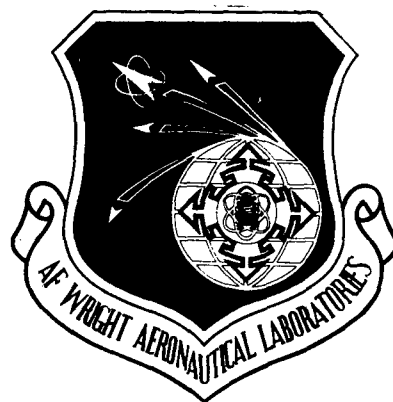


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## CHARACTERIZATION OF ACETYLENE TERMINATED SULFONE (ATS-G)

I. J. Goldfarb  
W. T. K. Stevenson

Polymer Branch  
Nonmetallic Division

May 1983

Final Report for Period January 1981 to December 1982

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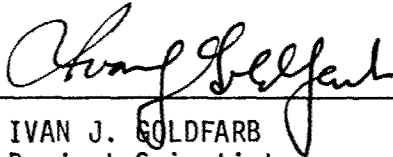
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) An acetylene terminated sulfone (ATS) mixture, prepared for the Air Force by Gulf Chemicals (ATS-G), was separated by column chromatography into its individual components which were characterized by spectroscopy and other common techniques of analysis. Cure reactions of ATS-G and its components were next examined by DSC and thermal stabilities by TGA.		

## FOREWORD

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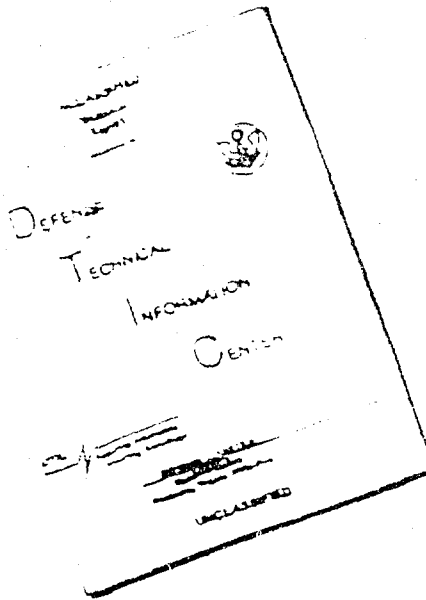
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## SECTION I

### INTRODUCTION

A considerable research effort is underway in this laboratory to evaluate a range of acetylene terminated prepolymeric materials which bulk polymerize to form stable, moisture resistant resins.

A novel synthetic route to one such prepolymer, acetylene terminated sulfone (ATS), was developed by the Gulf Chemical Company for the Air Force, (See Appendix). A large quantity of material was prepared for evaluation.

This report documents some chemical and thermal analyses of this material, (ATS-G).

## SECTION II

### SOLVENT ANALYSIS

In order to properly evaluate product distributions of degradation it was necessary to measure the solvent level in the prepolymer mixture. It must be emphasized that the following measurements only apply to the homogenized sample used throughout this work. Solvent levels will vary between batches of material.

#### 1. EFFICIENCY OF SOLVENT REMOVAL UNDER HIGH VACUUM CONDITIONS

Some solvents, for example toluene, can participate in chain transfer reactions with radical centers and, therefore, can alter modes of polymerization and degradation of polymers if they are present during polymerization and trapped in the material thereafter.

A typical TVA curve for solvent removal from ATS-G under high vacuum conditions is shown in Figure 1. It must be noted that rate profiles are dependent on sample film thicknesses which were kept constant for all TVA experiments.

Work performed in this laboratory (Reference 1) has shown that, at a programmed heating rate of 2°C/min, the quantity  $(T - T_g)$  for ATS-G is positive up to 200°C after which it changes sign and the polymer vitrifies. This crossover temperature will be higher for higher heating rates. Work in progress by I. J. Goldfarb indicates that the gel point of polymerization is reached at approximately 15 percent conversion. This corresponds to a temperature of 185°C at a heating rate of 5°C/min (Figure 2). A comparison between Figures 1 and 2 shows that, under high vacuum conditions, solvent is quantitatively removed before the onset of polymerization and therefore plays no part in either the polymerization or the degradation process.

## 2. QUANTITATIVE ESTIMATION

A solvent mixture, volatilized from ATS-G, was collected under high vacuum conditions and analyzed by SATVA (Figure 3).

Components of the mixture were identified by qualitative gas phase I.R. and proton N.M.R. spectroscopy.

With reference to the Appendix it can be seen that toluene is the incompletely removed solvent for Step 3 of the reaction. Diethynyl benzene (DEB) is produced by acetylations of excess m - dibromobenzene in Steps 2 and 3 of the reaction.

Toluene and diethynyl benzene were quantitatively estimated by collecting and analyzing solvent mixtures from the neat material using quantitative proton N.M.R. spectroscopy with methylene chloride as a marker (Table 1).

TABLE 1  
SOLVENTS VOLATILIZED FROM ATS-G

Sample Size	Wt. % Toluene	Wt. % Diethynyl Benzene (DEB)
500 mg	1.23	0.26
1.000 g	1.24	0.32

It must be emphasized that the estimated DEB concentration is a minimum value for the material as theoretically some may copolymerize with the ATS mixture on heating. In practice, however, the extent of copolymerization should be small.

The acetylene to toluene methyl group ratio in ATS-G was shown to be 27.0 to 1 by proton N.M.R. spectroscopy. Based on the analyses contained in this report it was calculated that 100.0 g of involatile material contains 0.370 mole equivalents of acetylene chain ends.

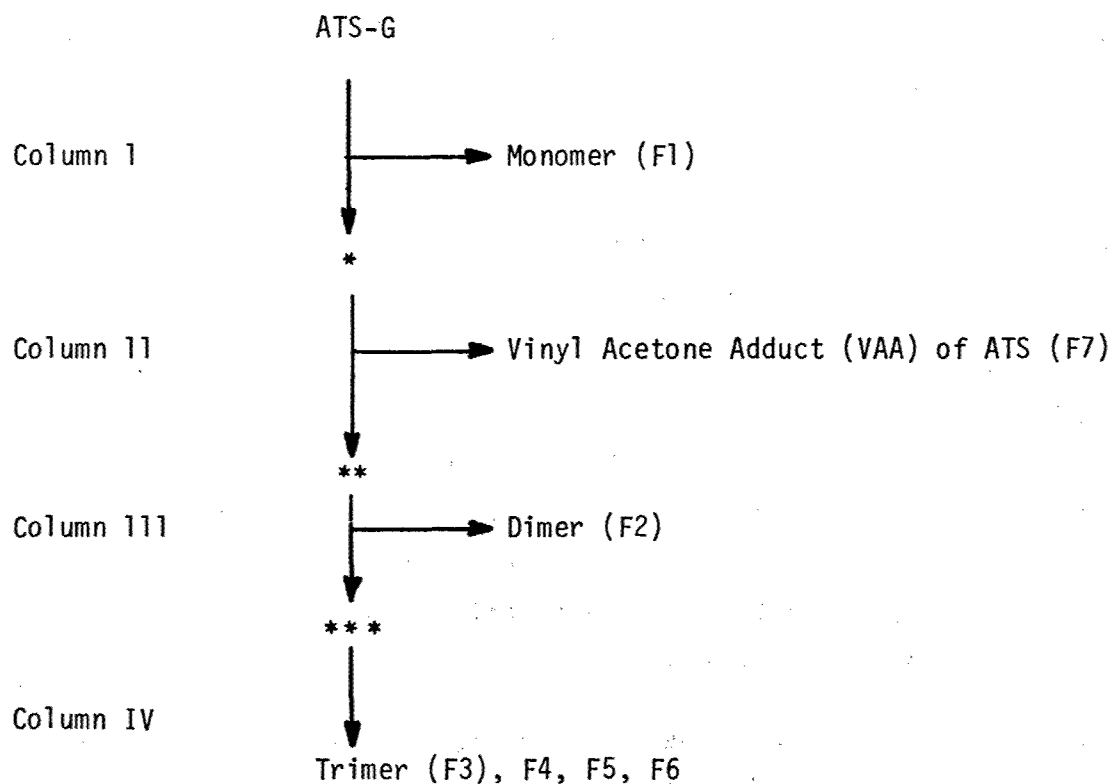
It can, therefore, be shown that 1.23 weight percent of the ATS-G mixture is toluene. This is in good agreement with the results of Table 1.

### SECTION III

#### CHROMATOGRAPHIC SEPARATIONS

The Gulf synthetic route always produces a mixture of monomer and higher oligomers in proportions which are dictated by the ratio of 1 to 2 in Reaction 1 (See Appendix). The mixture is made more complex by the presence of unreacted or partially reacted feedstock and the products of side reactions, some of which will be discussed in this report.

Components of the mixture were isolated using ad hoc chromatographic separations performed as shown below, freeze dried (when necessary), then vacuum dried at room temperature for several weeks before use.



#### 1. MONOMER ISOLATION (Table 2)

Column I - 3' x 5 cm, Regenerated SiO<sub>2</sub>

Solvent - Methylene Chloride

## Comments

a. Monomer was extracted as the only mobile component of the mixture. The column was stripped using THF to recover other material.

b. A small quantity of colored material was extracted along with the monomer. This material could not be identified because of its low concentration or removed by chromatographic methods.

TABLE 2

## COLUMN I SEPARATIONS

Run	Column Load (g)	% Recovery	Wt. % Monomer	Wt. % Other Material (*)
1	10.04	93.6	71.4	28.6
2	10.15	102.0	69.4	30.6
3	17.77	95.5	71.6	28.4
4	30.01	97.3	70.9	29.1
5	44.70	99.0	71.6	28.4
Average		<u>97.5</u>	<u>71.0</u>	<u>29.0</u>

## 2. VINYL ACETONE ADDUCT (VAA) ISOLATION (Table 3).

Column II - 3' x 5 cm, Regenerated SiO<sub>2</sub>

Solvent - Mixtures of Petroleum Ether and THF

## Comments

a. The column was first conditioned with petroleum ether after which mixtures of THF (30 Vol. % max.) and petroleum ether were used to extract mobile material.

b. VAA was isolated as the only immobile component in the column. It was recovered by stripping the column with pure THF.

TABLE 3

## COLUMN II SEPARATIONS

Run	Column Load (g)	% Recovery	Wt. % VAA	Wt. % Other Material (**)
A	7.44	101.0	20.3	79.7
B	8.00	100.0	18.4	81.6
C	9.56	102.0	16.5	83.5
Average		<u>101.0</u>	<u>18.4</u>	<u>81.6</u>

## 3. DIMER ISOLATION (Table 4)

Column III - 3' x 5 cm, Fresh SiO<sub>2</sub> with U.V. Indicator

Solvent - Methylene Chloride

## Comments

- a. Dimer was isolated as the first band eluted from the column.
- b. The column was then stripped of less mobile material with THF.

TABLE 4

## COLUMN III SEPARATIONS

Run	Column Load (g)	% Recovery	Wt. % Dimer	Wt. % Other Material (***)
I	4.00	104.0	69.0	31.0
II	5.41	105.0	65.0	35.0
Average		<u>104.5</u>	<u>67.0</u>	<u>33.0</u>

## 4. TRIMMER (F3), F4, F5 and F6 ISOLATION (Table 5).

Column IV - 3' x 5 cm, Fresh SiO<sub>2</sub> with U.V. Indicator

Solvent - 15% Diethyl Ether in Chloroform

## Comments

Fractions were eluted in the order F3, F4, F5 then F6.

TABLE 5  
COLUMN IV SEPARATION

Run	Column Load (g)	% Recovery	Wt. % F3	Wt. % F4	Wt. % F5	Wt. % F6
i	2.97	99	60	27	8	5

SECTION IV  
ELEMENTAL ANALYSES

Elemental analyses for F1 to F7 are shown in Table 6. Trace element concentrations were obtained by atomic absorption spectroscopy and are shown in Table 7.

TABLE 6  
ELEMENTAL ANALYSIS OF ATS-G AND ITS COMPONENTS

MATERIAL	%C	%H	%S	%O	%Br
ATS-B	75.50	3.775	6.92	13.80	0.75
F1	76.63	3.925	6.47	11.95	1.02
F2	73.40	3.82	7.75	14.19	0.84
F3	71.31	3.62	7.55	12.46	2.42
F7	74.505	5.30	6.07	12.14	1.98

The major element levels in ATS-G, F1, F2 and F3 are similar. The same fractions are shown to contain only small amounts of palladium and copper. The high hydrogen content of F7 indicates that it contains saturated material. Its sulphur content is below that of monomer. This indicates that its backbone is unlike that of normal ATS oligomers all of which have sulphur contents above that of monomer. Its high palladium content indicates that it is able to efficiently chelate the metal. The tabulated oxygen and bromine levels are inaccurate and will not be commented upon.

TABLE 7

## TRACE ELEMENT ANALYSIS OF ATS-G AND ITS COMPONENTS

Material	Pd (ppm)	Cu (ppm)	Si (ppm)
ATS-G	30.4	15	16
F1	<1.5	<0.5	16
F2	<1.5	1	22
F3	1.8	1	16
F4	3	x	x
F5	44	x	x
F6	166	x	x
F7	806	17	90

See Appendix

Copper is the incompletely removed catalyst for Reaction 1. Palladium is the incompletely removed catalyst for Reaction 2. Strong base is able to dissolve glass. Silicon may, therefore, have been added to ATS-G in Reaction 3. Some silica gel may also have been incorporated into F1 - F7.

## SECTION V

## GEL PERMEATION CHROMATOGRAPHY

ATS-G and its components were analyzed by GPC using a Waters associates LC instrument with microstyragel columns to yield the results shown below.

TABLE 8

## GPC ANALYSIS OF ATS-G AND ITS COMPONENTS

Material	Effective Hydrodynamic Radius, EHR ( $\text{\AA}$ )*	Comments
ATS-G	350	Composite Peak
F1	310	Single Peak
F2	600	Single Peak
F3	950	Single Peak
F4	480	Single Peak
F5	480	Single Peak
F6	600	Single Peak
F7	1300 (Major) 210, 65 (Trace Components)	Composite Peak**

\* Calibrated against polystyrene Standards

\*\* See Figure 4

The relative magnitudes of EHV for F1, F2 and F3 are close to those expected of ATS monomer, dimer and trimer. The F4 and F5 components are shown to be similar in size and somewhat larger than ATS monomer, while the F7 component is shown to be similar to ATS tetramer (if the trend exhibited by F1, F2 and F3 is continued).

The trace components of F7 were also isolated as constituents of the oligomeric or "cold ring" fraction of materials which are volatilized

from uncured ATS-G on programmed heating under high vacuum conditions (Reference 2). Together they were found to constitute 2.7 weight percent of the original material. The more abundant of the two (>90%) was found to be resorcinol while the less abundant material (<10%) was found to be phenoxy phenoxy phenol (probably m,m).

These materials are present in trace amounts in F7 (Figure 4) and so must be quantitatively lost in the course of separations I and II. It has been shown (Reference 3) that water can add to m - dibromobenzene in an Ullman ether side reaction. Resorcinol is the product of two such additions.

## SECTION VI

## INFRARED SPECTROSCOPY OF ATS-G AND ITS COMPONENTS

ATS-G, the acetone adduct of ATS monomer and F1 to F7 were analyzed as thin films cast from chloroform onto salt plates, using a Beckman I.R. 33 spectrometer. Spectra are shown in Figures 5-13.

All fractions contain aromatic material -  $3080\text{ cm}^{-1}$  (W), terminal acetylene groups -  $3300\text{ cm}^{-1}$  (S), sulfone -  $1290\text{-}1330\text{ cm}^{-1}$  (doublet S) and  $1090\text{-}1150\text{ cm}^{-1}$  (doublet S) and phenyl ether linkages -  $1240\text{ cm}^{-1}$  (broad S).

Fractions 4 - 7 produce "fingerprint" spectra very similar to monomer ATS (F1). Fractions 2 and 3 produce additional absorbance peaks at  $930\text{ cm}^{-1}$  and  $955\text{ cm}^{-1}$ . These may be assigned to  $-\text{SO}_2\text{SO}_2-$  linkages in both fractions.

Fractions 4 - 7 contain hydrogen bonded hydroxyl groups -  $3400\text{ cm}^{-1}$  (broad S). In addition, fractions 6 and 7 contain free hydroxylic material -  $3660\text{ cm}^{-1}$  (M).

Fractions 5 - 7 all produce a triplet of I.R. absorbances between  $2800\text{ cm}^{-1}$  and  $3000\text{ cm}^{-1}$  which are similar in position and relative intensity to those produced by the gem dimethyl groups of the acetone adduct of ATS monomer.

## SECTION VII

## PROTON MAGNETIC RESONANCE SPECTROSCOPY OF ATS-G AND ITS COMPONENTS

ATS-G, the acetone adduct of ATS monomer and F1 - F7 were analyzed by proton N.M.R. spectroscopy, in deuteriochloroform at room temperature, using a Varian EM 360, 60 MHz spectrometer. Spectra are shown in Figures 14-22. Signal integrations are reproduced in Table 9 where the following conventions are observed.

- A - Signal strength (8.1 - 7.8)  $\delta$ . Aromatic protons immediately adjacent to a sulfone linkage - 4 per linkage
- B - Signal strength (7.5 - 7.2)  $\delta$ . Aromatic protons (If separable from C)
- C - Signal strength (7.2 - 6.9)  $\delta$ . All other aromatic protons (If separable from B)
- D - Signal strength 3.1  $\delta$ . Acetylene protons
- E - Signal strength 2.25  $\delta$ . Saturated material (F7)
- F - Signal strength 1.45  $\delta$ . Saturated material (F7)

The ATS monomer fraction was contaminated with approximately four percent by weight benzene. The benzene signal added to the "B" integral. "B" was, therefore, assumed to equal "A".

If each sulfone group is surrounded by 4 "A" protons in a molecule containing 2 acetylene groups then a graph can be drawn to relate the A/D ratio to the sulfone content of the molecule (Figure 23). This rationale was applied to those fractions known to be 100% acetylene terminated to yield the results shown in Table 10.

TABLE 9

## PROTON N.M.R. PEAK INTEGRATIONS FOR ATS-G AND ITS COMPONENTS

Material		
ATS-G	A/(B + C)/D	1.00/3.48/0.39
AA	A/B/C	1.00/1.00/2.00
F1	A/B/C/D	1.00/1.00 <sup>*</sup> /2.10/0.52
F2	A/B/C/D	1.00/0.96/1.92/0.25
F3	A/(B + C)/D	1.00/2.68/0.167
F4	A/(B + C)/D	1.00/2.95/0.29
F5	A/(B + C)/D	1.00/3.03/0.19
F6**	A/(B + C)/D/E/F	1.00/3.37/0.25/0.44/2.63
F7	A/(B + C)/D/E/F	1.00/3.33/0.17/0.29/1.75

\* Assumed Value

\*\* Inaccurate

TABLE 10

## RELATIONSHIP OF A/D PROTON RATIOS TO SULFONE CONTENT

Material	A/D	Sulfones/Molecule	Comments
F1	1.92	1	ATS Monomer
F2	4.00	2	ATS Dimer
F3	5.99	3	ATS Trimer
F7	6.00	3	Like ATS Trimer

An extra phenoxy group can be incorporated into ATS-G and its components by the addition of water than m-dibromobenzene to a brominated chain end. The graphs shown in Figure 31 are used to relate the (B + C)/A ratio of each fraction to its extra phenoxy content in Table 11.

TABLE 11

## RELATIONSHIP OF (B + C)/A PROTON RATIOS TO PHENOXY CONTENT

Material	(B + C)/A Expected	(B + C)/A Found	Extra Phenoxy Content ( $\emptyset$ ) <sub>x</sub>
F1	3.00	3.10	x = 0.15
F2	2.50	2.88	x = 0.8
F3	2.33	2.68	x = 1.0
F4	?	2.95	
F5	?	3.03	
F7	2.33*	3.33	x = 3.0

\*Based on the results of Table 10.

The (B + C)/A ratios for F4 and F5 are close to 3.0 and indicate that both molecules possess a monomer backbone. The (B + C)/A ratio for F7 suggests that it contains 3 more phenoxy groups (or their equivalent) than F3. This can not be explained on the basis of an Ullman ether process.

The N.M.R. spectrum of F4 (3.1  $\delta$  triplet, 1.6  $\delta$  doublet, ratio 1 : 2) indicates that it contains abnormal acetone adduct chain ends of the type  $\text{H}-\text{C}\equiv\text{C}-\text{CH}_2-\underset{\text{OH}}{|}-$ .

A comparison of Figures 15 and 20 shows that F5 is the partially hydrolyzed acetone adduct of ATS monomer. The A/D ratio for this

fraction indicates that it is composed of a mixture of 24 percent di and 76 percent mono acetone adduct molecules.

The E and F singlet peaks of F7 show that it contains two deshielded and uncoupled saturated proton sites.

## SECTION VIII

### CARBON 13 N.M.R. SPECTROSCOPY OF ATS-G AND ITS COMPONENTS

Proton decoupled  $^{13}\text{C}$  N.M.R. spectra of ATS-G, F1, F2, F3 and F7 were obtained using a Varian XL-100 spectrometer.

Resonances in the spectra of ATS-G and F1 have been assigned to the appropriate carbon sites (Reference 4). Using this information it was possible to identify extra signals in the spectra of F2 and F3.

The spectrum of F7 in the region (100 - 200)ppm was similar to that of the other fractions except for an additional strong, protonated carbon signal at 125.3 ppm which could not be assigned to a normal ATS carbon site. In addition, F7 produced signals generated by saturated protonated carbons at 34.1 ppm (E), 30.3 ppm (F) and deshielded unprotonated carbons at 67.8 ppm.

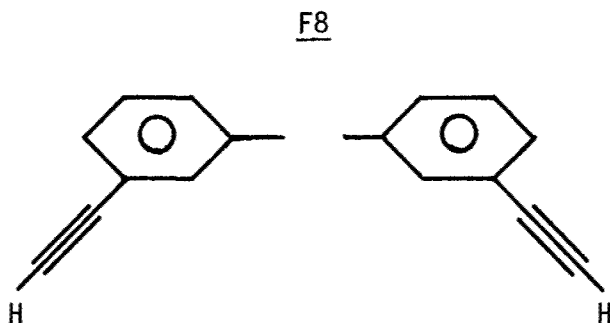
## SECTION IX

## ANALYSIS FOR 3,3'-bis DIETHYNYL DIPHENYLETHER DEDPE (F8)

A mixture of high molecular weight materials are volatilized from ATS-G on curing under high vacuum conditions. This mixture was separated by preparative TLC (silica gel /methylene chloride) into three fractions. The most mobile fraction was shown to account for approximately 0.1 percent of the initial sample weight. Identical material was subsequently isolated from uncured material using the same TLC system.

I.R. spectroscopy (Figure 25) was used to show the presence of unidentifiable saturated material, terminal acetylenes, phenyl ether linkages and m substituted aromatic material. GPC (Figure 26) and Chemical Ionization Mass Spectroscopy both identified one major component of the mixture (EHR - 120Å, 218 a.m.u.).

This material, 3,3'-bis diethynyl diphenyl ether, was formed by the the incorporation of an extra phenoxy group into DEB by the abnormal Ullman ether reaction discussed in Sections V and VII.



SECTION X  
STRUCTURE OF VAA (F7)

1. SUMMARY OF ANALYTICAL DATA

A Appearance - F7 is highly colored and, therefore, conjugated.

B Solubility - F7 is soluble in methylene chloride, chloroform, ethylene diamine and ether solvents. F7 is insoluble in carbon tetrachloride, benzene, toluene and water.

C TLC - F7 is polar or highly polarizable.

D GPC - F7 consists of one major component (EHR 1300 Å), and two trace impurities.

E Atomic Absorption Spectroscopy - F7 is able to efficiently chelate palladium and is the sole palladium carrier in ATS-G.

F I.R. Spectroscopy - F7 contains free and hydrogen bonded hydroxyl groups, gem dimethyl groups similar to those found in the acetone adduct of ATS monomer, and terminal acetylenes. Its molecular backbone is similar to that of ATS monomer.

G Proton N.M.R. Spectroscopy - F7 is 100% acetylene terminated. It contains three sulfone linkages per molecule and three more phenoxy groups (or their equivalent) than ATS trimer along with two deshielded gem dimethyl sites (E and F).

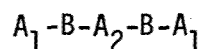
H Carbon 13 N.M.R. Spectroscopy - F7 contains an extra aromatic (or olefinic) type carbon site (F) not attributable to an ATS type backbone.

I Base Hydrolysis - Reaction 3 in the preparation of ATS-G was repeated. F7 in solution with toluene, and methylene chloride, was added to methanol and excess potassium hydroxide. The mixture was boiled to a sludge, base was removed, and the product mixture was examined by I.R. and N.M.R. spectroscopy. Both the soluble and insoluble fractions

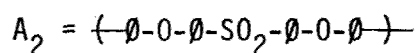
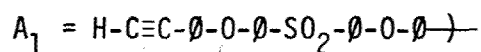
were shown to be identical to the starting material except for the loss of some acetylene chain ends by polymerization. F7 was, therefore, shown to be stable to base hydrolysis.

## 2. PROPOSED STRUCTURE OF VAA (F7)

The following structure is proposed.



where:

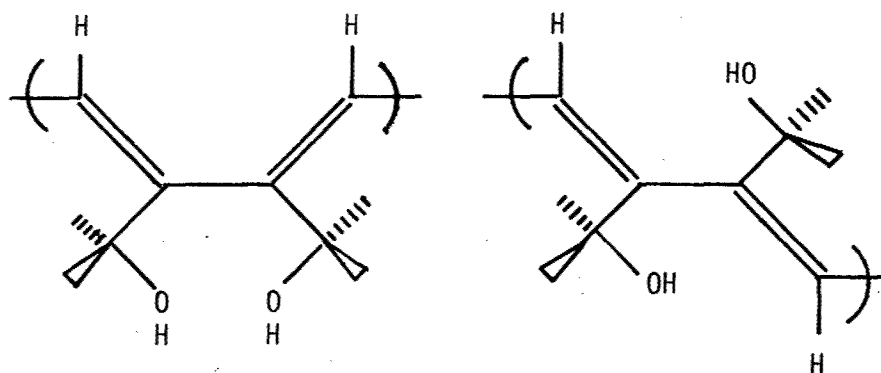


And B =

"E"

OR

"F"



This structure was supported by the proton N.M.R. peak ratios shown in Table 12.

TABLE 12

## A COMPARISON BETWEEN EXPECTED AND FOUND PROTON RATIOS FOR VAA (F7)

Ratios	Expected	Found
A/(B + C)/D/(E + F)	1.00/3.33/0.16/2.00	1.00/3.33/0.16/2.00

The anomalous results of Table 11 can, therefore, be explained. F7 contains two phenoxy groups and four aromatic type protons or the "equivalent" of three more phenoxy groups than ATS trimer.

## SECTION XI

### THERMAL DEGRADATION OF VAA (F7)

An insight can often be gained into the structure of complex materials by the use of techniques of thermal degradation.

The TVA/ATVA/SATVA system (Reference 2) was used in conjunction with programmed TGA in an attempt to examine the thermal stability of VAA and obtain information to support the structure proposed in Section X.

#### 1. THERMAL VOLATILIZATION ANALYSIS (TVA)

A TVA trace for F7 is shown in Figure 27. Solvent (THF) is volatilized from the sample which thereafter degrades in four steps. Steps 2, 3 and 4 produce condensable and noncondensable material via processes similar to those which decompose ATS monomer and dimer. Step 1 is unique to this system and produces condensable material.

#### 2. SUB AMBIENT THERMAL VOLATILIZATION ANALYSIS (SATVA)

The condensable volatile fraction of degradation to 1018°C was collected and separated by SATVA (Figure 28). Components of the mixture were identified by gas phase I.R. and proton N.M.R. spectroscopy. The product distribution was similar to that for ATS monomer and dimer with the addition of propene and butadiene.

The condensable volatile products of Steps 1, 2 and 3 were examined by SATVA (Figures 29, 30 and 31). Butadiene is produced in Step 1 and propene in Step 3 of the degradation process.

#### 3. QUANTITATIVE VOLATILE PRODUCT ANALYSIS

It was shown by TGA (Figure 54) that F7 loses 13 percent of its initial weight on curing at 5°C/min, due to evaporation of THF, resorcinol and phenoxy phenoxy phenol all presumably hydrogen bonded to the VAA group. Using the remainder as a base weight for the material (871%)

the weight percentages of some products of degradation were measured using quantitative gas phase I.R. spectroscopy (Table 13).

TABLE 13  
QUANTITATIVE DEGRADATION PRODUCT ANALYSIS FOR VAA (F7)  
AND ATS MONOMER

<u>Product</u>	<u>Wt.% of F7</u> (corrected for solvent loss during curing)	<u>Wt.% of ATS Monomer</u> (corrected for solvent and monomer loss during curing)
CO	9.2	7.4
CH <sub>4</sub>	2.1	3.6
CO <sub>2</sub>	3.7	1.2
SO <sub>2</sub>	11.7	11.4

The methane and sulfur dioxide yields from F7 and ATS monomer are similar. In contrast, the CO<sub>2</sub> and CO yields from F7 are larger than those from mono ATS. The former is a result of a similarity of backbone structure while the latter is a result of the higher oxygen content of F7.

#### 4. BUTADIENE YIELD

With reference to Figure 54 it can be shown that a sample of F7 loses 10 percent of its initial weight during Step 1 of degradation between 250°C and 390°C. The only materials lost in this process are sulfur dioxide and butadiene. A 100 mg sample was shown by quantitative gas phase I.R. spectroscopy to produce 4.0 mg of sulfur dioxide in this temperature interval. As such the butadiene yield was shown to be 6.0 mg. The maximum yield of butadiene from this material is  $\frac{(54 \times 2 \times 87)}{1586}$  mg or 5.9 mg. The close agreement between the expected and found butadiene yields supports the proposed structure of F7.

Materials of molecular weight in the region of 500 a.m.u. are volatile under high vacuum conditions in the temperature range (283 - 391)°C.

The A<sub>2</sub> segment of F7 constitutes approximately 30 percent by weight of the material. A simple scission process would volatilize approximately 40 percent of the sample. The A<sub>1</sub> and A<sub>2</sub> segments must, therefore, quantitatively recombine in Step 1 of degradation.

#### 5. RESIDUE AND OLIGOMERIC PRODUCT ANALYSIS

The weight percentage of the residue of degradation of F7 to 1018°C in the TVA apparatus was shown to be similar to that of other ATS type polymers (Table 14).

The I.R. and N.M.R. spectra of the oligomeric product fraction of degradation of F7 are shown in Figures 46 and 47 and indicate that its composition is similar to that of the oligomeric product fraction of degradation of ATS-G, ATS monomer and ATS dimer (Reference 2).

TABLE 14  
RESIDUES OF DEGRADATION TO 1018°C OF AT TYPE POLYMERS

Material	Wt.% Residue (Corrected for solvent and oligomer loss during curing)
ATS-G	53.2
ATS Monomer	54.5
ATS Dimer	49.6
F7	48.7

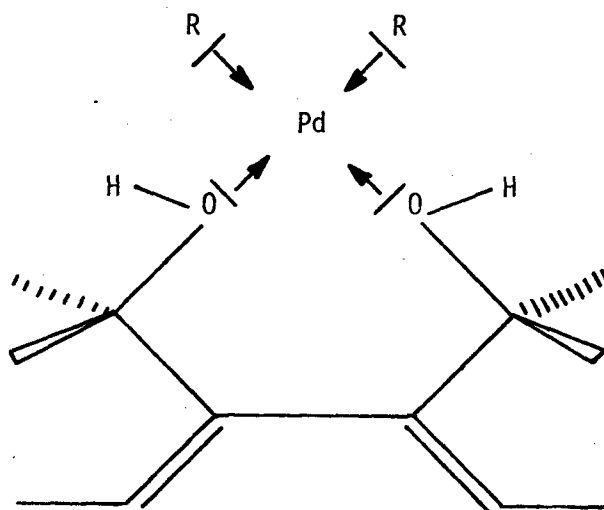
#### 6. SUMMARY

The thermal breakdown of F7, especially the butadiene yield, supports its proposed structure. Step 1 of degradation was shown to remove butadiene from the polymer. Steps 2, 3 and 4 decompose the residue of Step 1 in a manner similar to Steps 1, 2 and 3 of normal ATS type polymers (Reference 2). Step 3 of decomposition produces propene by degradation of the isopropanol derivatives produced in Step 1 of degradation.

## SECTION XII

## COMPLEXATION OF PALLADIUM WITH VAA (F7)

The low palladium levels of F4 and F5 show that palladium does not efficiently complex with isolated hydroxyl groups. For this reason it must be assumed that palladium chelates with the cis diene linkage of F7 in a square planer complex which contains 2 other electron donating ligands (R).



The E/F proton n.m.r. ratio in F7 is 0.17/1, 14.5 percent of the "B" linkages are, therefore, "cis" and 85.5 percent are "trans" in nature.

F7 was shown by TGA to contain 13 percent by weight of solvent. If this is taken into account, the palladium content of the vinyl acetone adduct (VAA) molecule is 926 ppm. Using this figure it can be shown that 5.1 percent of the "cis" linkages are complexed to palladium.

### SECTION XIII

#### REMOVAL OF PALLADIUM FROM VAA (F7)

Palladium is removed from ATS-G in the final stages of preparation by extraction with diethylamine. Two situations are possible. The diethylamine may extract the palladium - VAA complex which is insoluble in toluene (the solvent used in this step) and soluble in diethylamine, or it may break the palladium - VAA "bond" and chelate the metal itself.

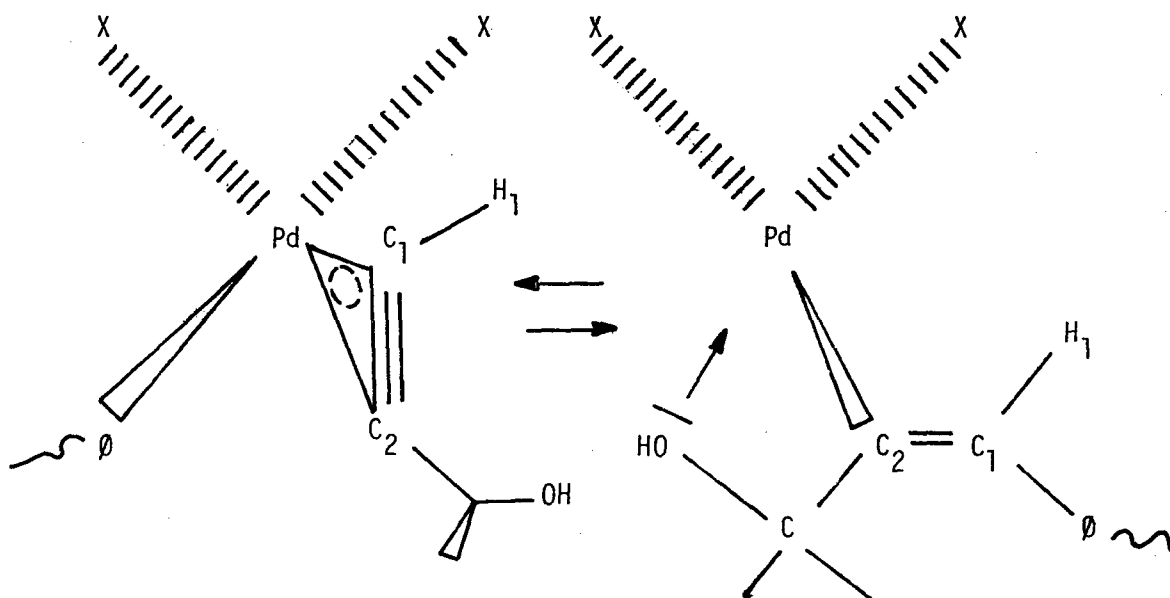
F7 was dissolved in diethylamine. The solution was warmed to 60°C, cooled to room temperature and painted across a preparative TLC plate which was developed with water to remove diethylamine. F7, which is immobile in this system, was recovered using THF and analyzed by A.A. spectroscopy. Its Pd content dropped to 62 ppm to show that diethylamine chelates the metal itself.

## SECTION XIV

## PROPOSED SOURCE OF VAA (F7)

The transition complex in the formation of the acetone adduct of ATS is possibly of the form:

(Appendix - Reaction 2)



The X ligands are halogen atoms and  $\emptyset$  is the terminal benzene of a sulfone molecule, minus the bromine which may occupy one of the "X" positions in the complex. The rate determining step in the formation of the acetone adduct group is probably the removal of the electron deficient  $H_1$  atom by a halogen ligand to form an acidic gas (HX). This would increase the electron density on  $C_1$ , promote the formation of a  $C_1 - C_2$  triple bond and expel the adduct from the complex.

If both halogens are replaced by a second pair of reactants  $H_1$  cannot be removed. A  $C_2 - C_2$  bond forming reaction would produce instead the vinyl acetone adduct (VAA) linkage. The cis linkage would be produced if the stability generated by intramolecular hydrogen bonding could lower

its free energy below that of the more thermodynamically stable trans linkage. In Section XII, 14.5 percent of linkages were shown to be "cis" and 85.5 percent were shown to be "trans". As such, steric and Van der Waals repulsions must be more dominant.

Molecules which contain one such VAA linkage (F6) would be expected to be more plentiful than those which contain two (F7). This situation is reversed in the ATS-G mixture. It must, therefore, be concluded that the mono adduct (F6) was quantitatively removed from the mixture during work up.

## SECTION XV

## COMPOSITION OF ATS-G

The percentage composition of ATS-G was calculated using the results of Sections I - XIII and is shown in Table 15.

TABLE 15

## PERCENTAGE COMPOSITION OF ATS-G

<u>Component</u>	<u>Wt.% of ATS-G</u>
Toluene	1.2
DEB	0.3
Resorcinol	2.7
ATS Monomer (F1)	67.7
ATS Dimer (F2)	15.2
ATS Trimer (F3)	4.5
F4 (Mixture of anomalous monomeric species)	2.0
F5 (Partially hydrolyzed AA)	0.6
F6 (Mono VAA)	0.4
VAA (F7) + Solvent	5.1
DEDPE (F8)	0.1

## SECTION XVI

## DSC OF ATS-G AND ITS COMPONENTS

Qualitative DSC measurements were performed using a Du Pont 990 instrument package. Cure kinetics were obtained using a Perkin Elmer DSC - 2 instrument interfaced with a Bascom Turner minicomputer.

## 1. DSC OF ATS-G AND ITS COMPONENTS

Qualitative DSC curves for ATS-G and its components, cured at a heating rate of 10°C/min under nitrogen, are shown in Figures 34-42. Melting points ( $T_m$ ) of the uncured material were identified as sharp low temperature endotherms which did not change the baseline of the scan. Glass transition temperatures ( $T_g$ ) of the cured and uncured materials were interpreted as onset temperatures of baseline changes the latter often being accompanied by a broad hysteresis endotherm. All cure processes produced DSC exotherms. All systems were shown to undergo one or more post cure reactions. Major points of interest are summarized in Table 16. Unmeasurable or uncertain quantities are identified by the letter "X".

The ATS monomer fraction was recovered as a tacky, viscous material from which solvent could not be efficiently removed by pumping under vacuum. The material was, therefore, freeze dried and recovered as a fine powder. On storage over a period of months the material regained its initial form. All other fractions were recovered as fine powders which did not flow on storage at room temperature. The ATS monomer fraction is, therefore, the only component with room temperature "tack and drape". This is probably a result of its low  $T_g$ .

TABLE 16  
DSC OF ATS-G AND ITS COMPONENTS

--- °C ---

Material	T <sub>m</sub>	Initial T <sub>g</sub>	Cured* T <sub>g</sub>	T (max) Polymerization	T (max) Post Cure Reaction
ATS-G	X	X	X	215	360 (Exo)
F1	57	-14	320	223	395 (Exo)
F2	69	53	234	225	390 (Exo)
F3	X	80	225	214	340 (Exo)
F4	X	43	225	202	305,340 (Exo)
F5	X	57	205	225	X
F7	X	55	247	215	350 (Endo)

\*Scan 1 to 450°C may allow some degradation to take place. This will lower the "Cured" T<sub>g</sub> below its ideal value.

The rate profiles for F5 and F7 (Figures 41 and 42) can be interpreted either in terms of two exotherms or one broad exotherm with an overlapping endotherm. The (apparent) low temperature rate maxima and minima for F5, (147, 170)°C and F7 (155, 170)°C, are close to initial and rate maxima temperatures for weight loss from these materials (Figures 53 and 54). The latter explanation is, therefore, preferred.

The post cure exotherms of ATS-G and F1 - F3 are probably produced by thermal isomerizations of the polyene chain to a most stable configuration.

The cured T<sub>g</sub>'s of fractions 2 - 7 are all between 200 and 250°C. As expected, the T<sub>g</sub> of ATS monomer is higher than that for ATS dimer, which

is in turn higher than that for ATS trimer. The Tg's of F4 and F5 are low because these materials are only partially acetylene terminated and begin to decompose at temperatures above 150°C. The cured Tg of F7 would be expected to be lower than that of F3 on the basis of molecular size and expected cross link density. With reference to Section XI it can be shown that the 350°C post cure endotherm for this material corresponds to Step 1 of degradation, in which butadiene linkages are quantitatively removed from the polymer. The higher Tg for cured F7 is evidence that Step 1 of degradation extensively cross links the material.

## 2. KINETIC ANALYSIS OF ATS-G AND ITS COMPONENTS

The cure reaction of ATS-G, ATS monomer, ATS dimer and ATS trimer were examined by DSC. Materials were cured at six different heating rates to produce rate data which was analyzed by the Friedman method (Reference 5) using a computer program developed at AFWAL/MBP (Reference 6). Some kinetic and thermodynamic parameters are summarized in Table 17.

TABLE 17

### KINETIC AND THERMODYNAMIC PARAMETERS FOR THE CURE REACTION OF ATS-G AND ITS COMPONENTS

Material	Heat of Reaction (cal/g)	Corrected for Solvent Loss (cal/g)	Effective Molecular Weight	Heat of Reaction (Kcal/mole) H	Activation Energy E
ATS-G	115.95	117.72	488 <sup>(1,2)</sup>	57.45	21.304
F1	132.01	141.95	464 <sup>(2)</sup>	65.86	21.306
F2	79.29	80.50	848 <sup>(2)</sup>	68.26	22.681
F3	62.04	63.31	1190 <sup>(2)</sup>	75.34	17.315

#### KEY

(1) Number average molecular weight  $M_n$ , ( $\Sigma M^* X^*$ ) - Table 15.

(2) Includes extra phenoxy material - Table 11.

Values of  $E$  were combined with other kinetic parameters to construct Arrhenius type rate equations which were used to produce reaction window plots for 5, 50 and 95 percent cure (Figures 43, 44, 45 and Reference 6). The relative isothermal reactivity of each system is inversely proportional to its activation energy of polymerization ( $E$ ) as expected.

The activation energy for polymerization of ATS-G is similar to that for mono ATS (F1). This shows that the addition of F2 - F8 to ATS monomer, in the amounts shown in Figure 15, does not alter its rate profile of polymerization. Corresponding molar heats of polymerization do, however, differ, to show that the addition to ATS monomer of F2 - F8 changes its mechanism of polymerization.

The activation energy and heat of polymerization of the ATS trimer component are abnormally low and high (respectively) in comparison with corresponding values for the ATS monomer and dimer fractions. This can only be explained if the ATS trimer component contains a radical promoter other than palladium which accelerates the polymerization reaction. A comparison of reaction window plots shows that its effect on the polymerization reaction is most marked at low temperatures and extents of conversion. This "promoter", which may be an abnormal chain end or a molecular weak link, is probably responsible for the low temperature "shoulder" on the polymerization exotherm of the ATS trimer component (Figure 39).

## SECTION XVII

## THERMOGRAVIMETRY OF ATS-G AND ITS COMPONENTS

## 1. ISOTHERMAL LOW TEMPERATURE TGA in AIR

The long term stabilities of ATS-G, ATS monomer and ATS dimer in air at 260°C and 316°C were compared using isothermal TGA (Reference 7).

Samples were precured by programmed heating at 5°C/min to 234°C under high vacuum conditions, placed in the isothermal aging apparatus and heated in air at 260°C for 200 hr then at 316°C for 200 hr to yield the weight loss curves shown in Figures 46 and 47. No noticeable differences in stability between the three fractions were observed. The initial drop in sample weights at 260°C, probably due to loss of moisture, is followed by a 200 hr period in which the samples gain then lose a few percent of weight by reaction with oxygen. All three samples are stable in air at 260°C; 40 percent (by weight) is, however, volatilized from all three samples after 200 hr at 316°C. Oxygen may or may not be involved in this process.

## 2. PROGRAMMED TGA UNDER HELIUM

ATS-G and its components were degraded under programmed conditions at 5°C/min to 1000°C under Helium in a Du Pont 990 thermoanalyzer. Weight loss and rate curves are shown in Figures 48-54. Solvent compensated weight loss curves are compared in Figure 55.

## a. Weight Loss During Curing

The extents of volatilization of ATS-G and the ATS monomer fraction on curing at 5°C/min under high vacuum conditions were examined gravimetrically in the TVA apparatus and are compared in Table 15 with corresponding weight losses under Helium. The values of column 4 are close to those of column 5 to show that a helium atmosphere suppresses the evolution of high molecular weight (or boiling point) materials from ATS type systems during curing under programmed conditions.

Samples of ATS-G cured under nitrogen or air must, therefore, contain 2.7 weight percent resorcinol trapped in the polymer network (Table 15).

TABLE 18

A COMPARISON BETWEEN WEIGHT LOSS DURING CURING OF ATS-G  
AND ATS MONOMER UNDER HIGH VACUUM CONDITIONS AND UNDER A  
HELIUM ATMOSPHERE

Material	Vacuum				(←Helium→)
	Film Thickness (μm)	Wt.% Volatilization	Wt.% High** Molecular Wt. Material	Wt.%* Solvent	Wt.% Volatilization
ATS-G	95	7.2	5.7	1.5	1.5
	240	5.2	3.7	1.5	
ATS Monomer	95	17.4	12.3	5.1	7.0

#### KEY

\* Unaffected By Film Thickness

\*\* Inversely Proportional to Film Thickness

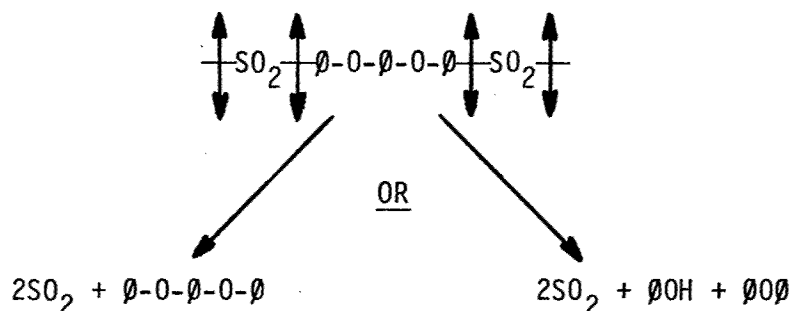
#### b. Weight Loss by Degradation (Figure 62, Table 19).

ATS-G and its components were all shown to degrade in a two step process. Approximately (30 - 40)% of each polymer is volatilized in the temperature range (400 - 600)°C producing sulfur dioxide, carbon dioxide, COS, H<sub>2</sub>S, benzene, water, phenol and some oligomeric material in an SO<sub>2</sub> initiated scission process which partially volatilizes the sample leaving polyene centered aromatic clusters which fuze above 600°C to produce carbon monoxide, methane and hydrogen and a final residue which is composed almost completely of carbon (Reference 2).

Fractions 4 and 5 are partially volatilized in the temperature range (150 - 400)°C in a process which is probably initiated by thermal decompositions of residual acetone adduct groups in the polymer matrix. Fraction 7 (VAA) is partially volatilized in the temperature range (390 - 450)°C by thermal decompositions of vinyl acetone adduct linkages.

The stabilities of F1 - F3 with respect to Step 1 of degradation increase with polyene concentration (or cross link density) in the polymer matrix. The behavior of F4 - F7 cannot be compared in this manner because of extra low temperature processes of degradation which must be taken into consideration. Stabilities to 600°C are in the order F1>F2>F3>F4>F5>F7. The order of stability with respect to Step 2 is similar except that F3 and F4 exchange positions. ATS-G is shown to be less stable than ATS monomer but more stable than ATS dimer to thermal degradation.

Fractions 2 and 3 are more stable than could be expected with respect to stage 1 of degradation if the sulfone - sulfone linkage were to be quantitatively volatilized as shown below.



A majority of radicals produced by SO<sub>2</sub> scissions must, therefore, terminate to produce involatile material.

TABLE 19  
TGA OF ATS-G AND ITS COMPONENTS UNDER HELIUM  
— °C —

Material	Degradation Commences	Bulk Degradation Commences	Approximate Rate Max.	Bulk Degradation Ends
ATS-G	375	435	525	600
F1	410	460	525	590
F2	360	475	545	590
F3	310	475	535	590
F4	160	435	500	X
F5	150	425	485	X
F7	290	290/445	350/500	X

## SECTION XVIII

## CONCLUSIONS

ATS-G is best considered as a blend of ATS monomer with a mixture of acetylene terminated aromatic impurities. The effects of these impurities on the system are best evaluated by comparing the behavior of ATS-G with that of its ATS monomer component. Some of the conclusions refer to this comparison.

1 ATS-G is composed of a mixture of ATS monomer, at least 10 other fractions, and trace quantities of palladium, copper and silicon.

2 Toluene, DEB, resorcinol and DEDPE are efficiently removed from thin films of ATS-G, cured under high vacuum conditions. Toluene and DEB are efficiently removed from thin films of ATS-G, cured under nitrogen. It is unlikely that any of these components are efficiently removed from films of the thicknesses required to make composites. They are, therefore, incorporated or trapped in ATS-G resin on curing and may effect its subsequent performance.

3 The structures of F1, F2, F3, F5, F6, F7 and F8 have been elucidated. F4 is shown to be composed of mixtures of ATS monomer ATS molecules, partially end capped with acetylene groups and with acetone adduct groups, some of which may be abnormal in structure.

4 Water is shown to be incorporated into ATS-G by an Ullman ether coupling reaction. Other hydroxylic material may also be incorporated to form weak links in the polymer.

5 Palladium is chelated to cis VAA groupings in F6 and F7. The complex may promote polymerization in ATS-G by complexing with acetylene chain ends and influencing mechanisms of polymerization or by acting as a radical source to initiate polymerization.

6 F2 - F7 begin to polymerize at lower temperatures than F1. Their presence in the mixture encourages low temperature polymerizations by

processes which become less important at high conversions to polymer. The cure reaction of F3 can only be explained by assuming that it contains a radical source. F4 and F5 must also produce radicals at abnormally low temperatures, presumably via a low temperature "tail" of the process which causes measurable volatilizations above 150°C. F7 contains palladium, a promoter of AT polymerizations. It may also contain material similar to that which promotes low temperature polymerizations in F3 - F5.

7 The "post cure" reaction in ATS-G is assumed to be the process in which the polymer is heated close to or above its ultimate Tg to complete the polyene cluster network. Decompositions of the F4, F5 and F7 components in this temperature range may effect this process and, therefore, the ultimate mechanical properties of the resin.

8 Long term aging experiments show that low temperature weight loss from ATS-G is identical to that from its monomer and dimer components. The rate of decomposition at these temperatures in air is, therefore, effected neither by cross link density nor impurities present in the ATS-G system.

9 ATS-G is shown by programmed TGA to be less stable at high temperatures than its monomeric component but more stable than its dimeric component to thermal degradation. The stability of all ATS-G component polymers appears to increase with polyene concentration or cross link density although a direct comparison of the stability of all fractions is not possible. A large proportion of the radicals produced by sulfone scissions in ATS polymers are shown (by deduction) to terminate, forming involatile material.

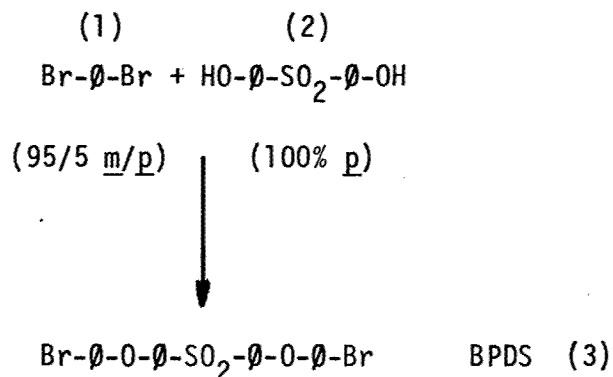
APPENDIX

PREPARATION OF ATS-G (Reference 8)

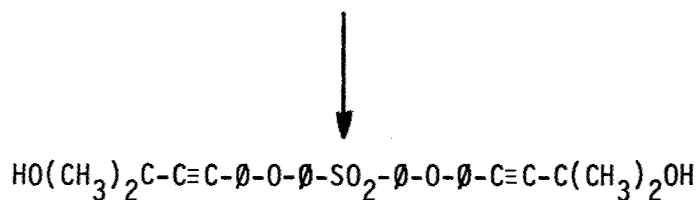
## PREPARATION OF AST-G (Reference 8)

MONOMER PREPARATION

Reaction 1a An Ullman Ether Condensation of Dibromobenzene (1) and Sulfonyldiphenol (2).

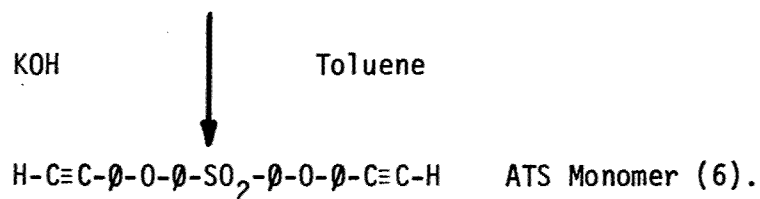


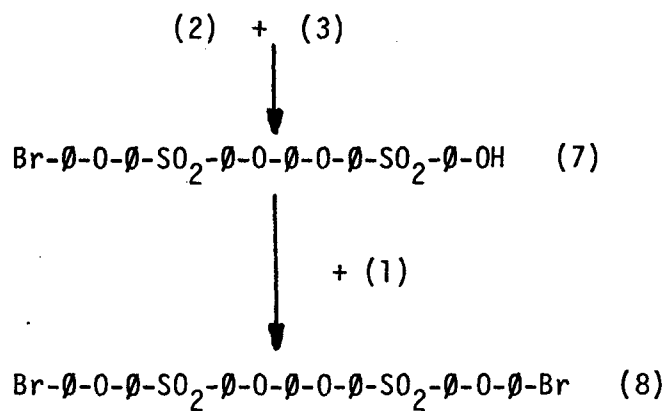
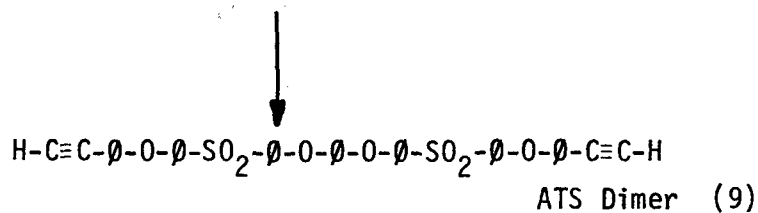
Reaction 2a The Replacement of Bromine by 2-Methyl-3-butyn-2-ol (4) In the Presence of a Palladium Catalyst.



The Acetone Adduct of ATS Monomer (5).

Reaction 3a A Base Promoted End Group Cleavage of (5).



DIMER PREPARATIONReaction 1bReactions 2 and 3,b

Trimer and higher oligomers are obtained by reapplying reactions 1, 2 and 3,b to (8).

ILLUSTRATIONS

1 - 55

Heating rate 5°C/min

Sample size 101 mg

Film thickness 95  $\mu\text{m}$

KEY

- Material Volatile at 0°C
- - - Material Volatile at -75°C
- + - Material Volatile at -196°C
- + + +

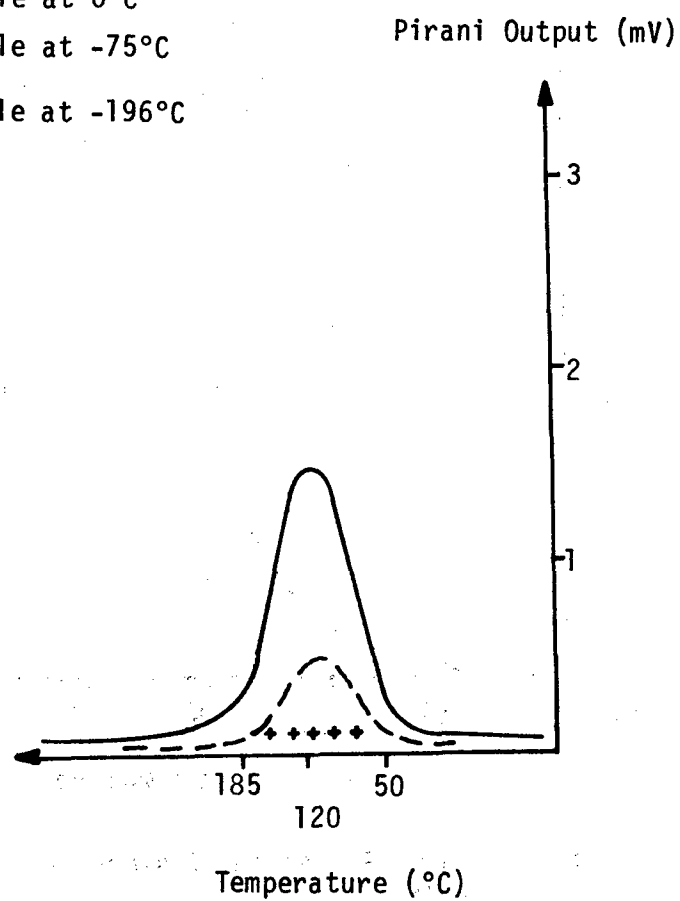


Figure 1. Thermal Volatilization Analysis (TVA) of Solvent Removed From ATS-G by Heating Under High Vacuum Conditions

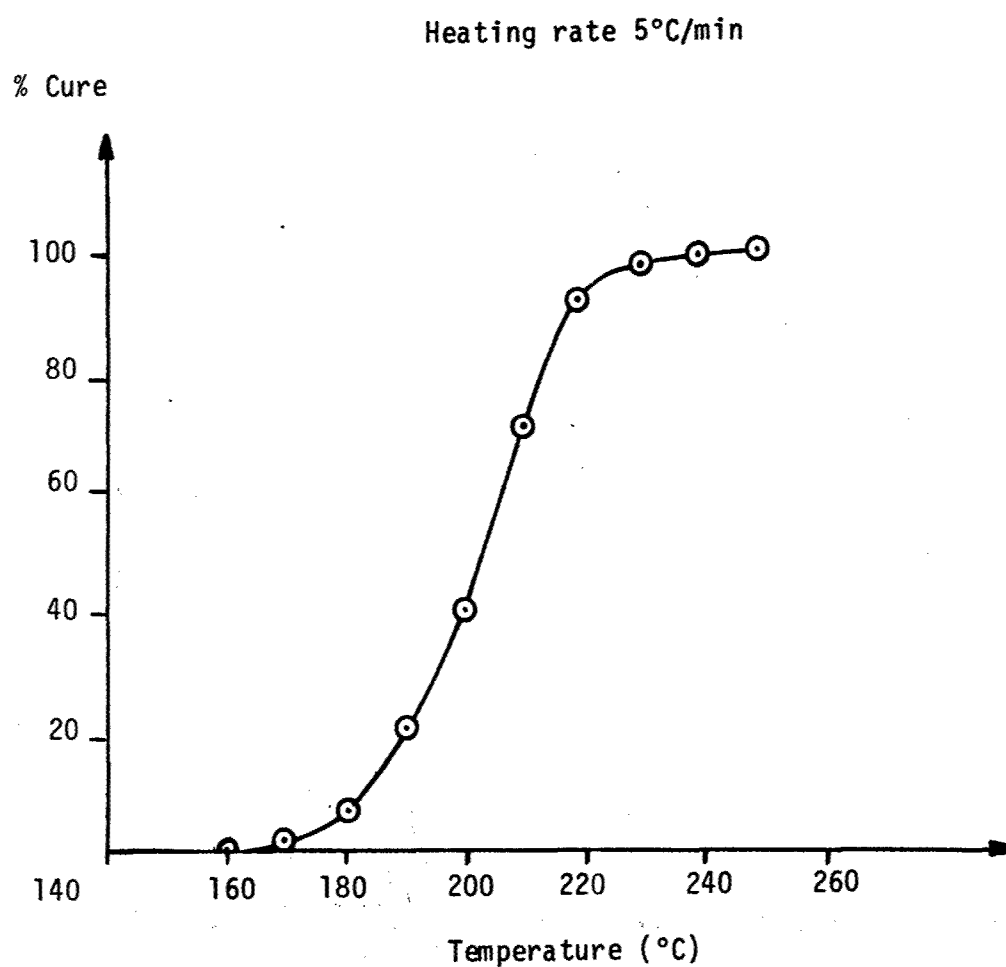


Figure 2. ATS-G, Percentage Conversion to Polymer vs Temperature by DSC

Sample size 104 mg

KEY

- ( - ) Thermocouple Output (Trap temperature)
- Pirani Output (Pressure)
- 1 Chloroform (Film Casting Solvent)
- 2 Toluene
- 3 Diethynylbenzene (DEB)

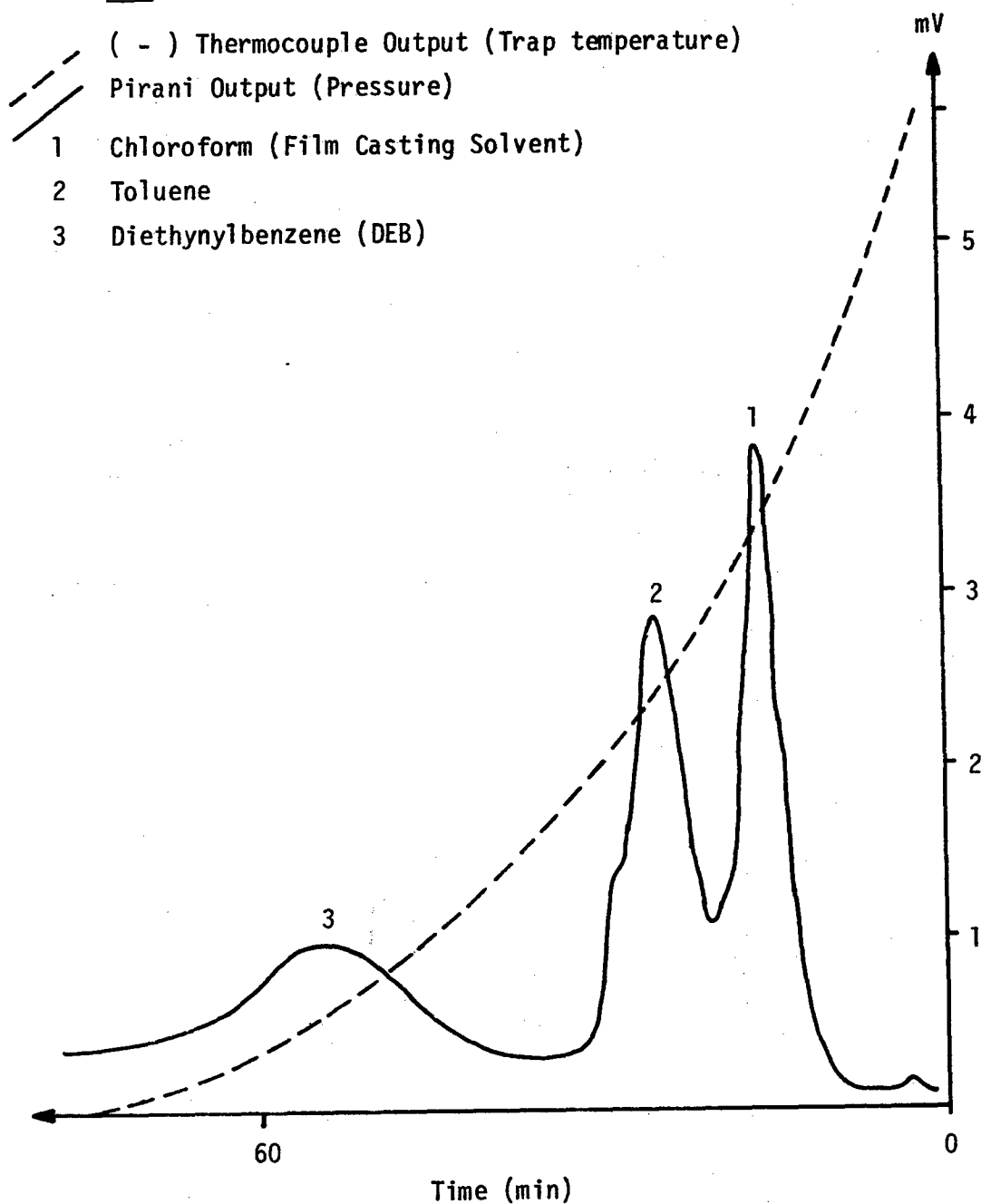


Figure 3. Sub Ambient Thermal Volatilization Analysis (SATVA) of Solvents Removed From ATS-G by Heating Under High Vacuum Conditions to 234°C

Solvent THF

Flow rate 2.5 ml/min

KEY

1/

EHR 1300Å

RV 30.63 ml

RT 12.25 min

2/

EHR 210 Å

RV 38.13 ml

RT 15.25 min

3/

EHR 65Å

RV 43.13 ml

RT 17.25 min

U.V. Absorbance At 254 nm

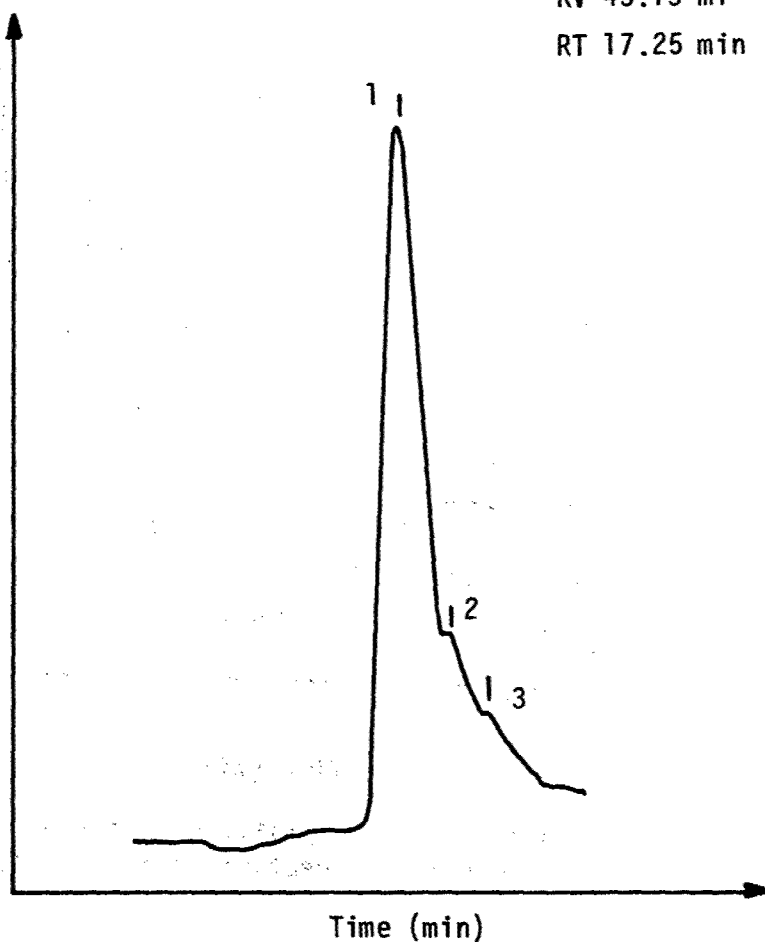


Figure 4. GPC Analysis of VAA (F7)

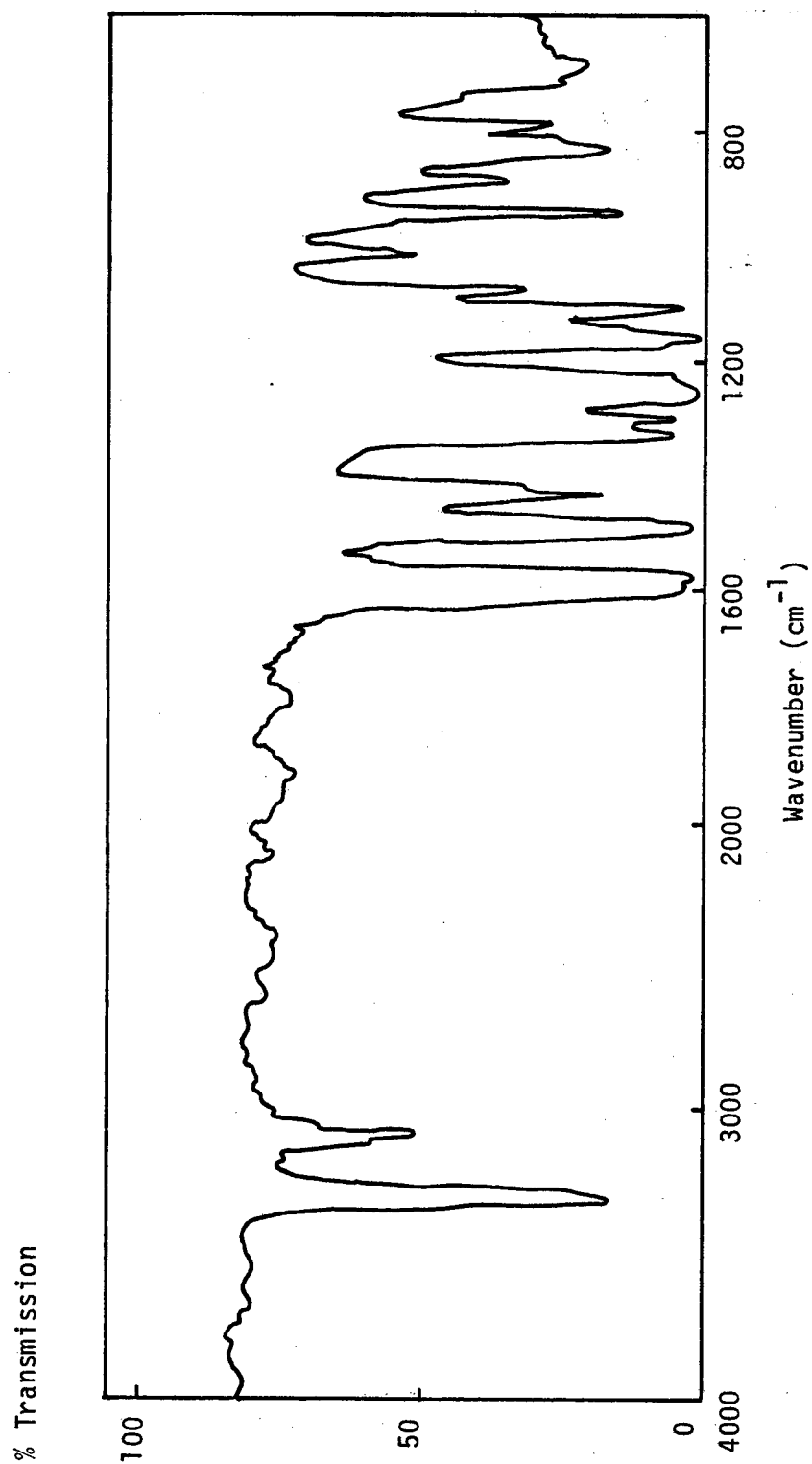


Figure 5. I.R. Spectrum of ATS-G

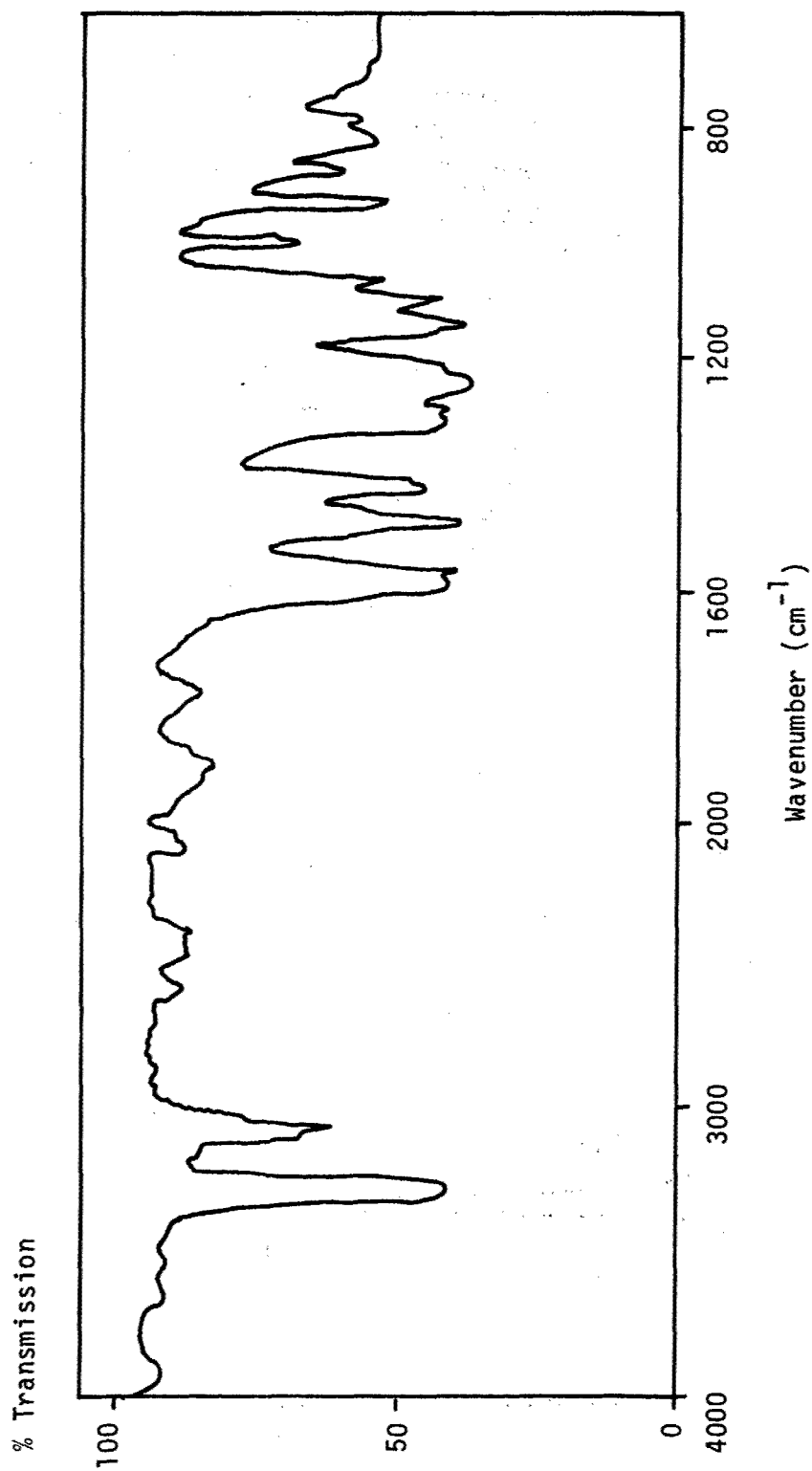


Figure 6. I.R. Spectrum of the Acetone Adduct of ATS Monomer

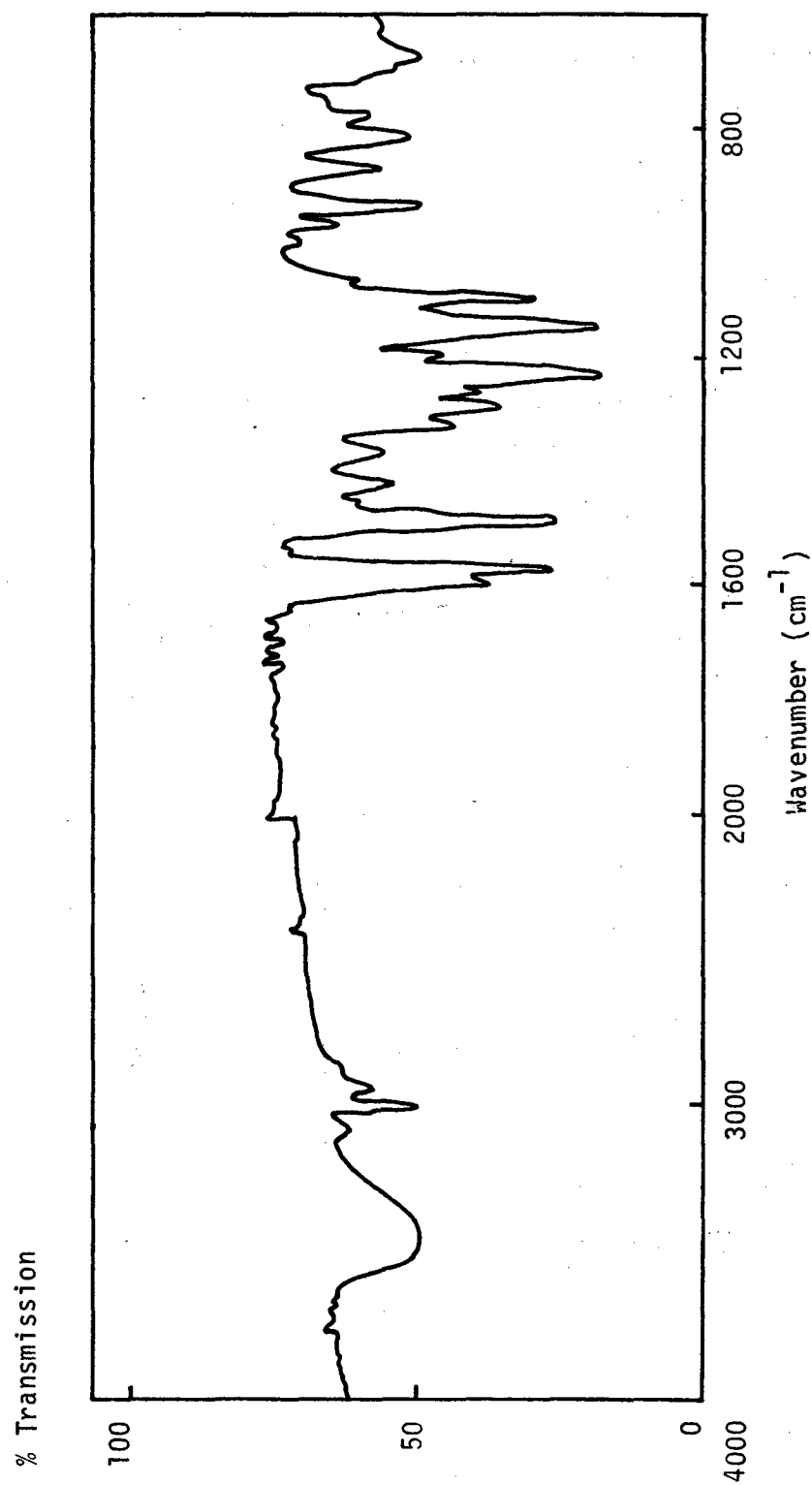


Figure 7. I.R. Spectrum of ATS Monomer (F1)

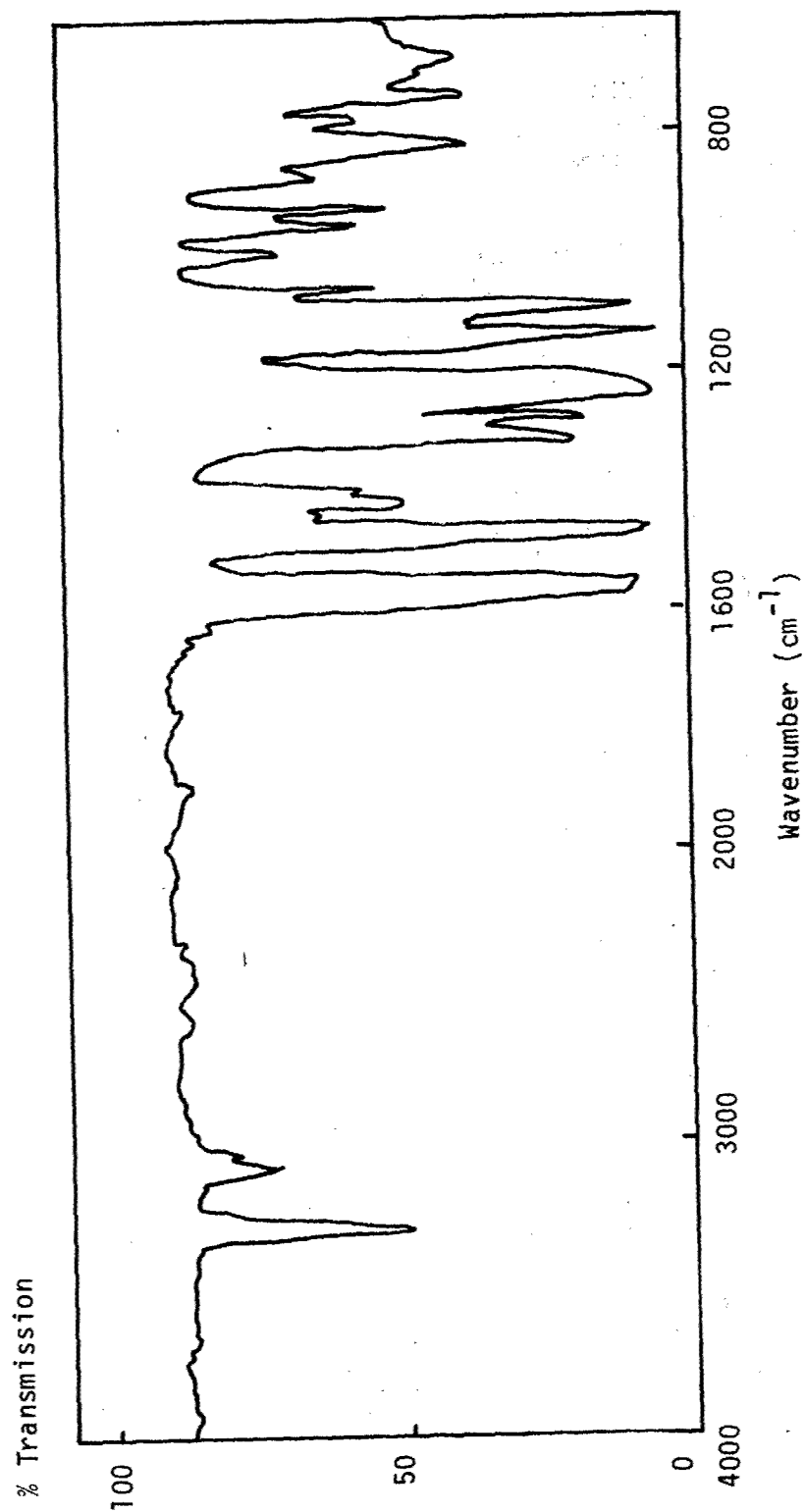


Figure 8. I.R. Spectrum of ATS Dimer (F2)

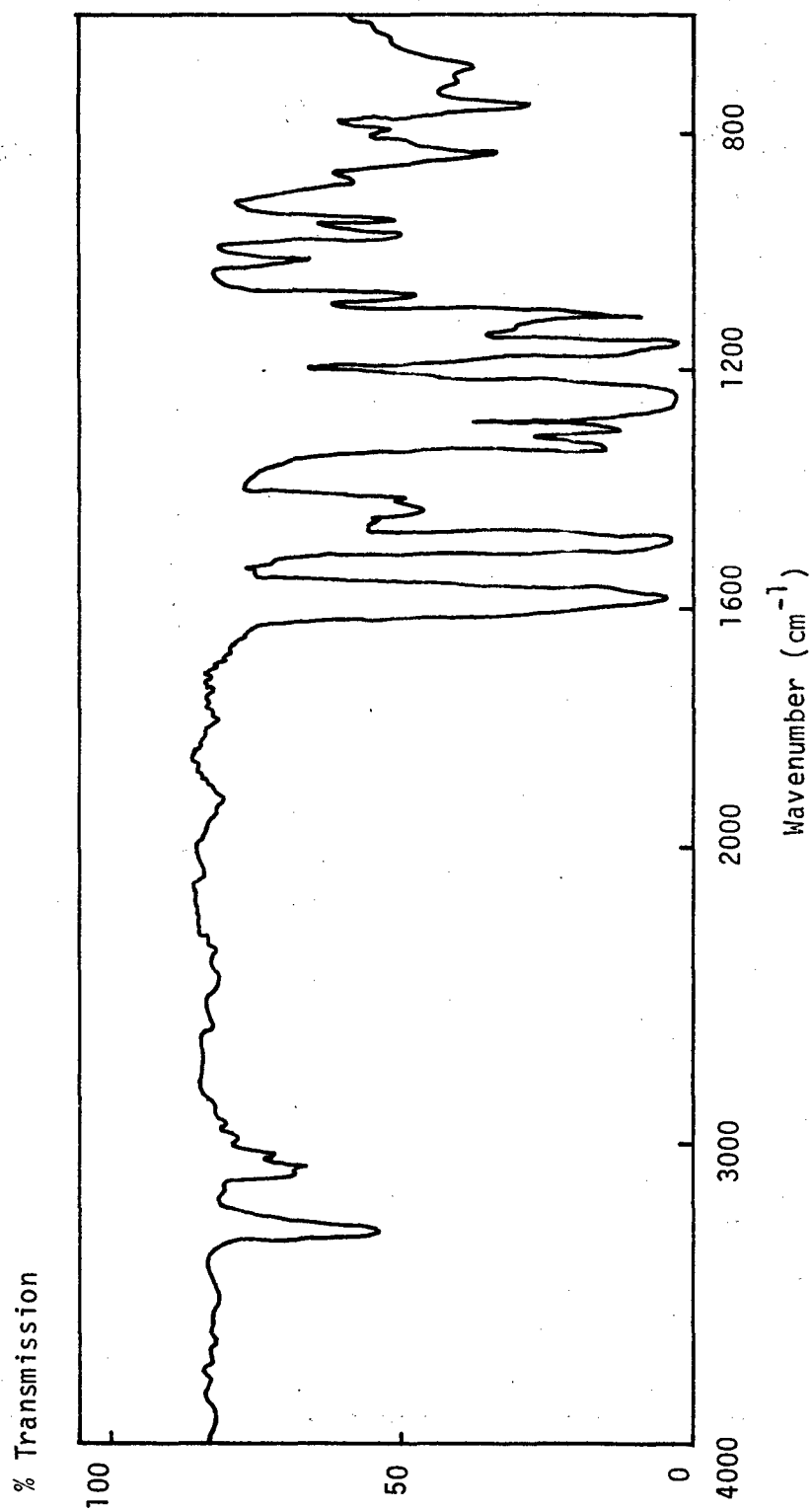


Figure 9. I.R. Spectrum of ATS Trimer (F3)

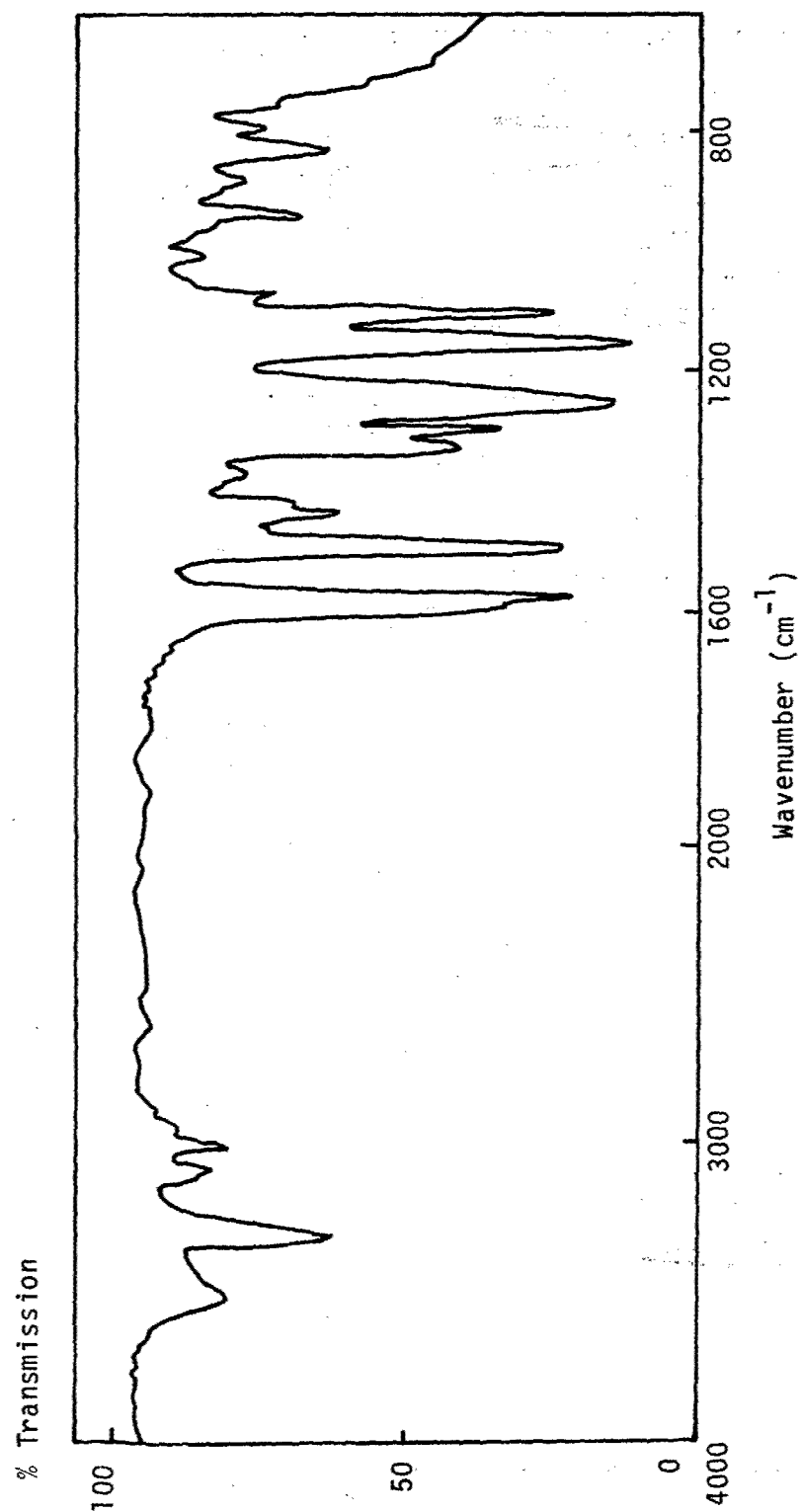


Figure 10. I.R. Spectrum of F4

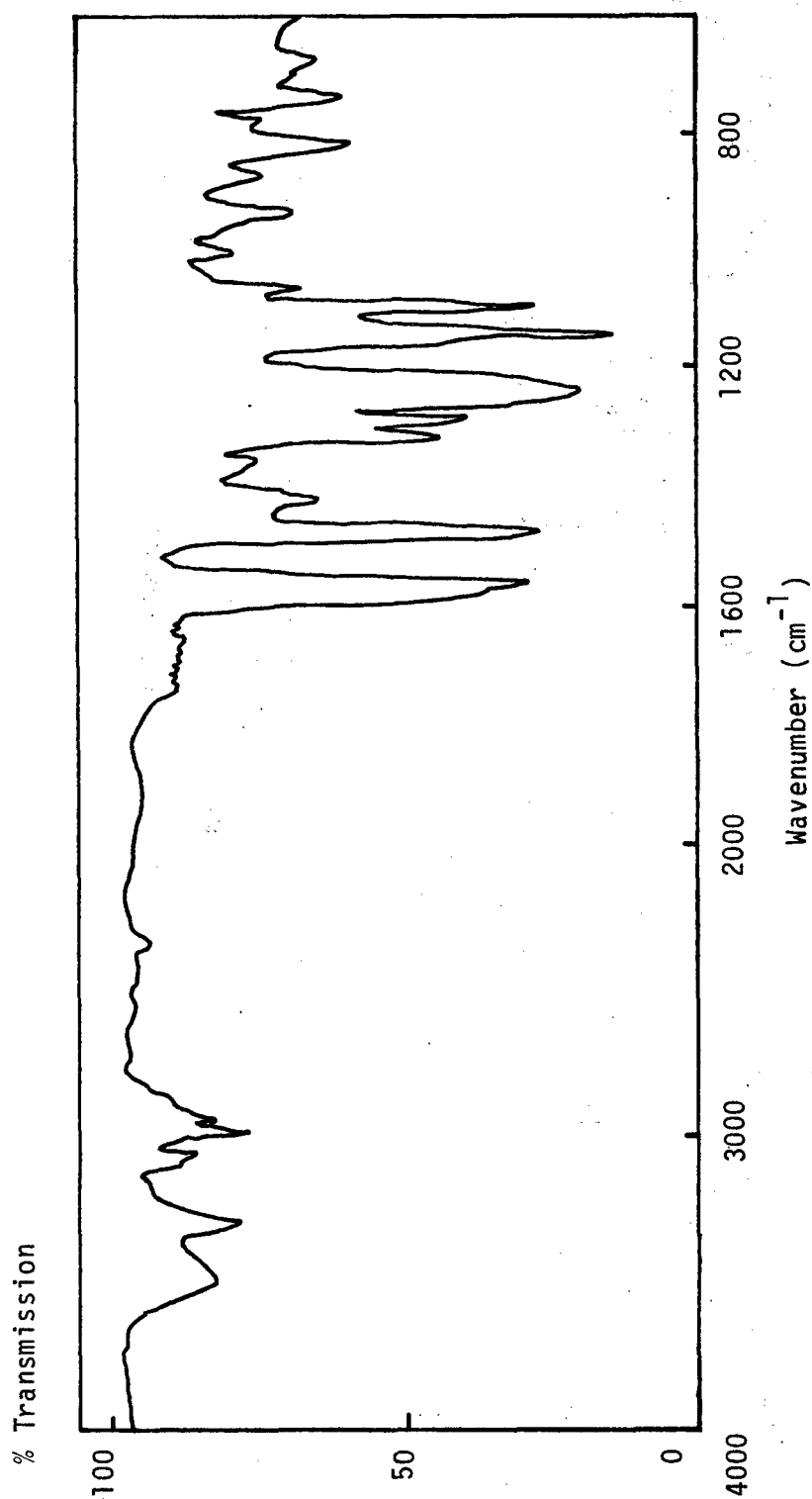


Figure 11. I.R. Spectrum of F5

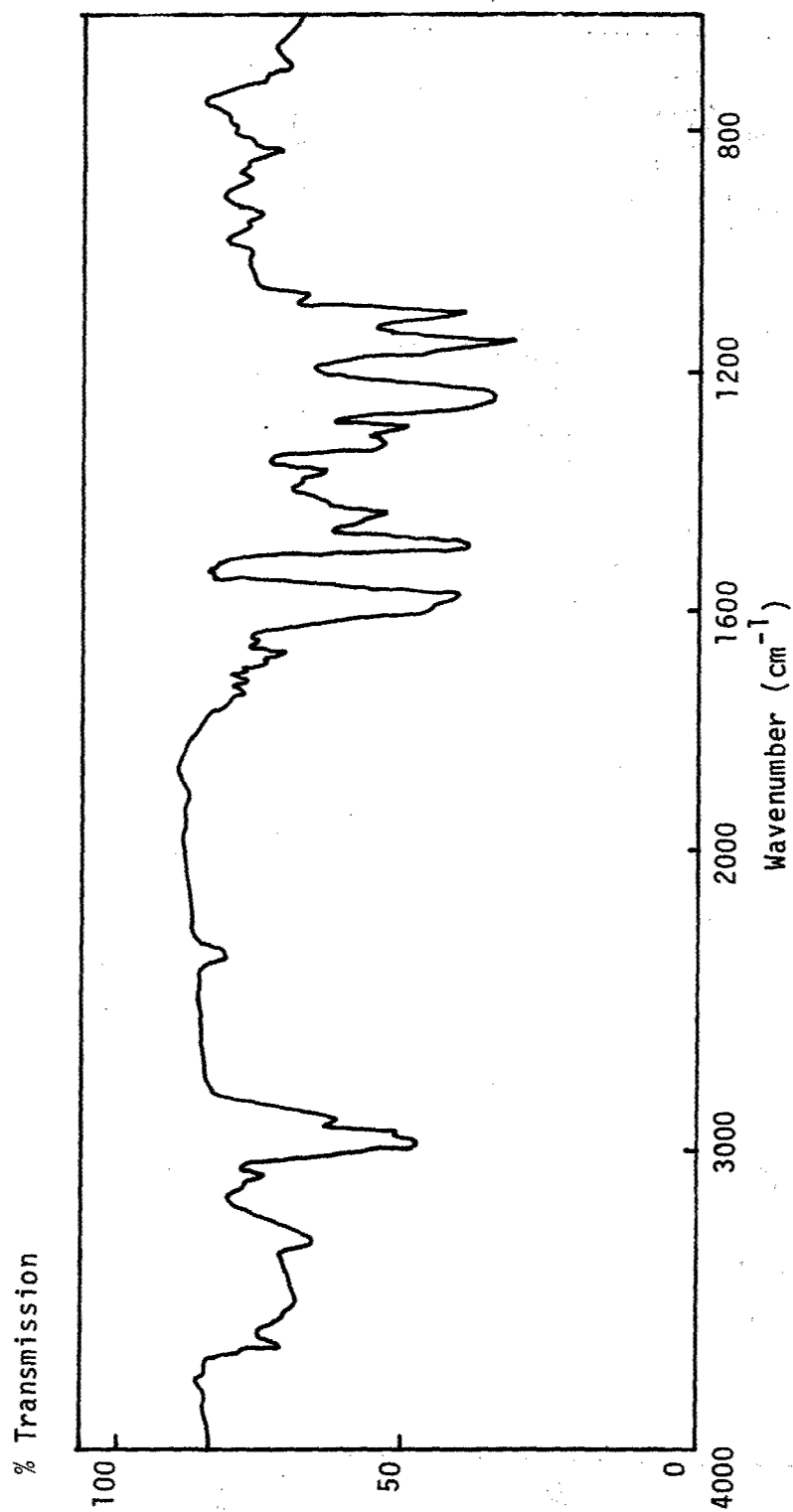


Figure 12. I.R. Spectrum of F6

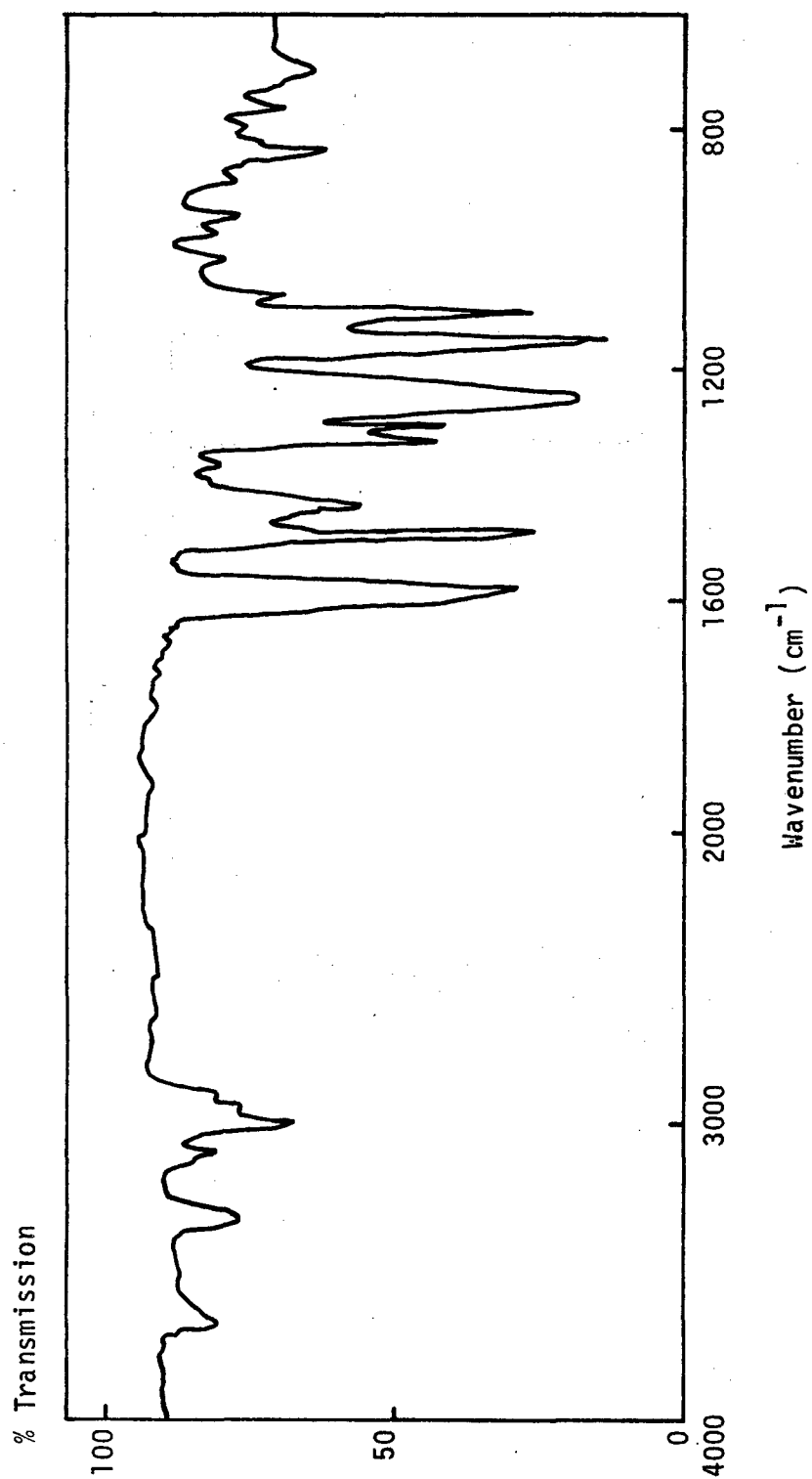


Figure 13. I.R. Spectrum of VAA (F7)

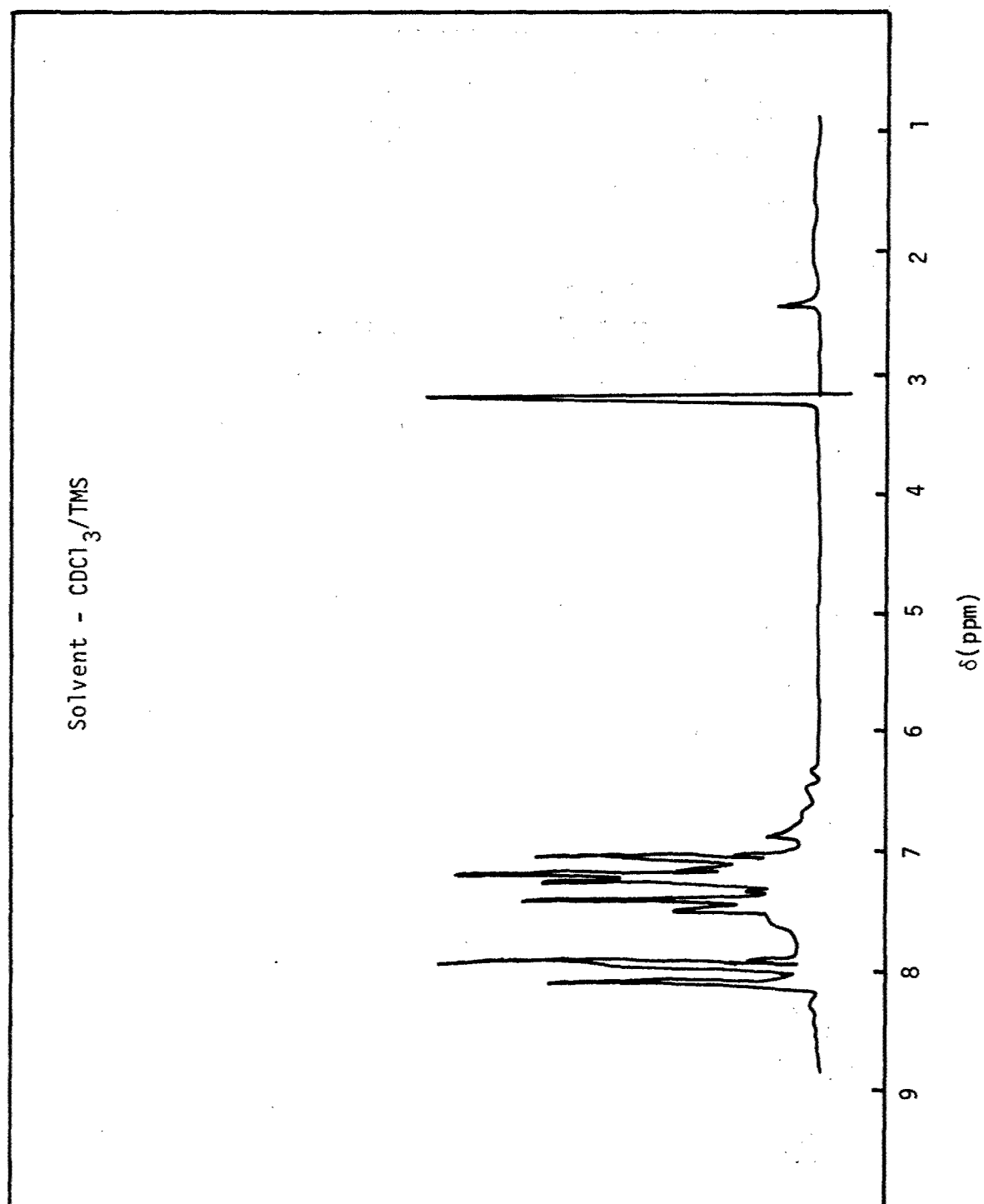


Figure 14. Proton N.M.R. Spectrum of ATS-G

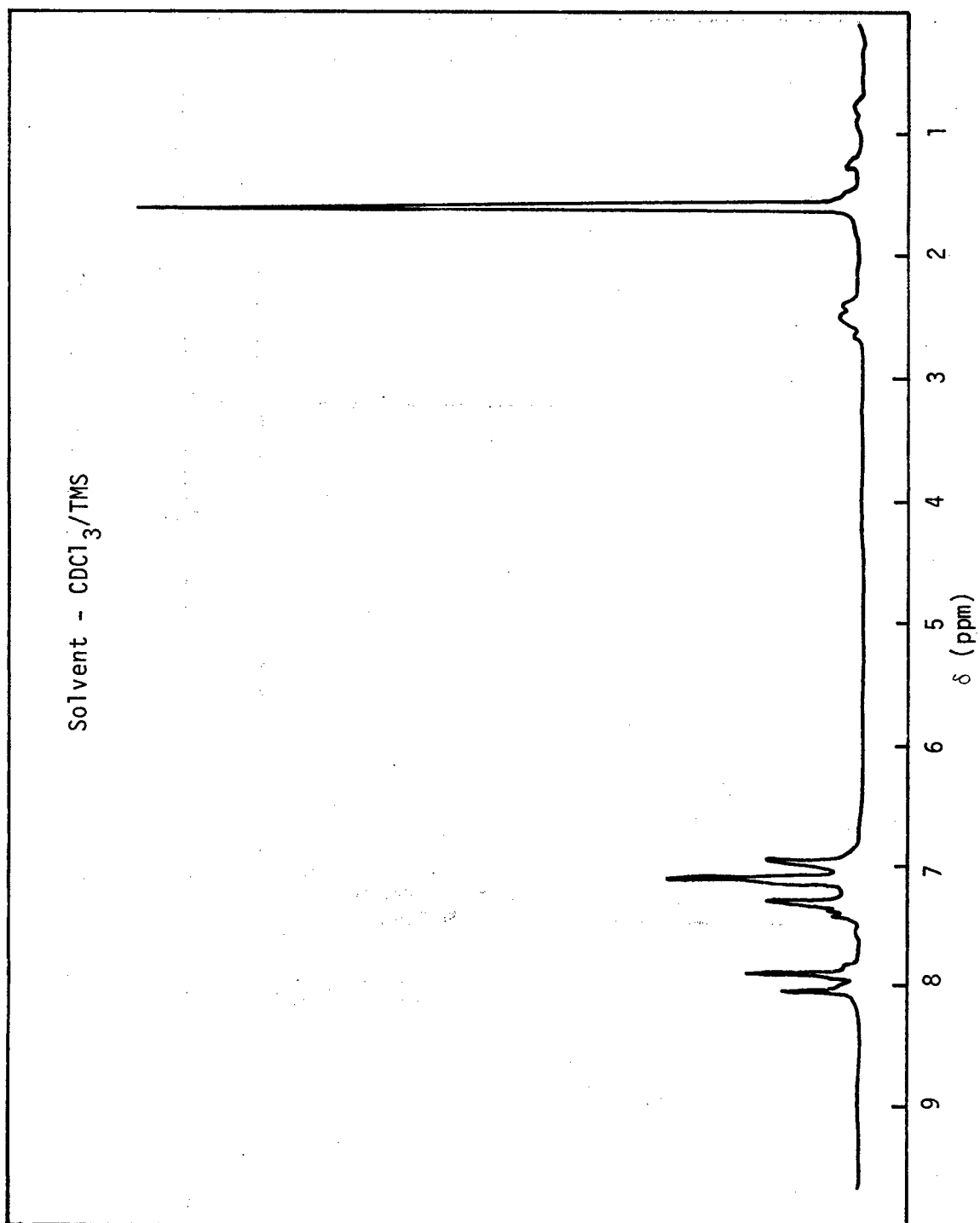


Figure 15. Proton N.M.R. Spectrum of the Acetone Adduct of  
ATS Monomer

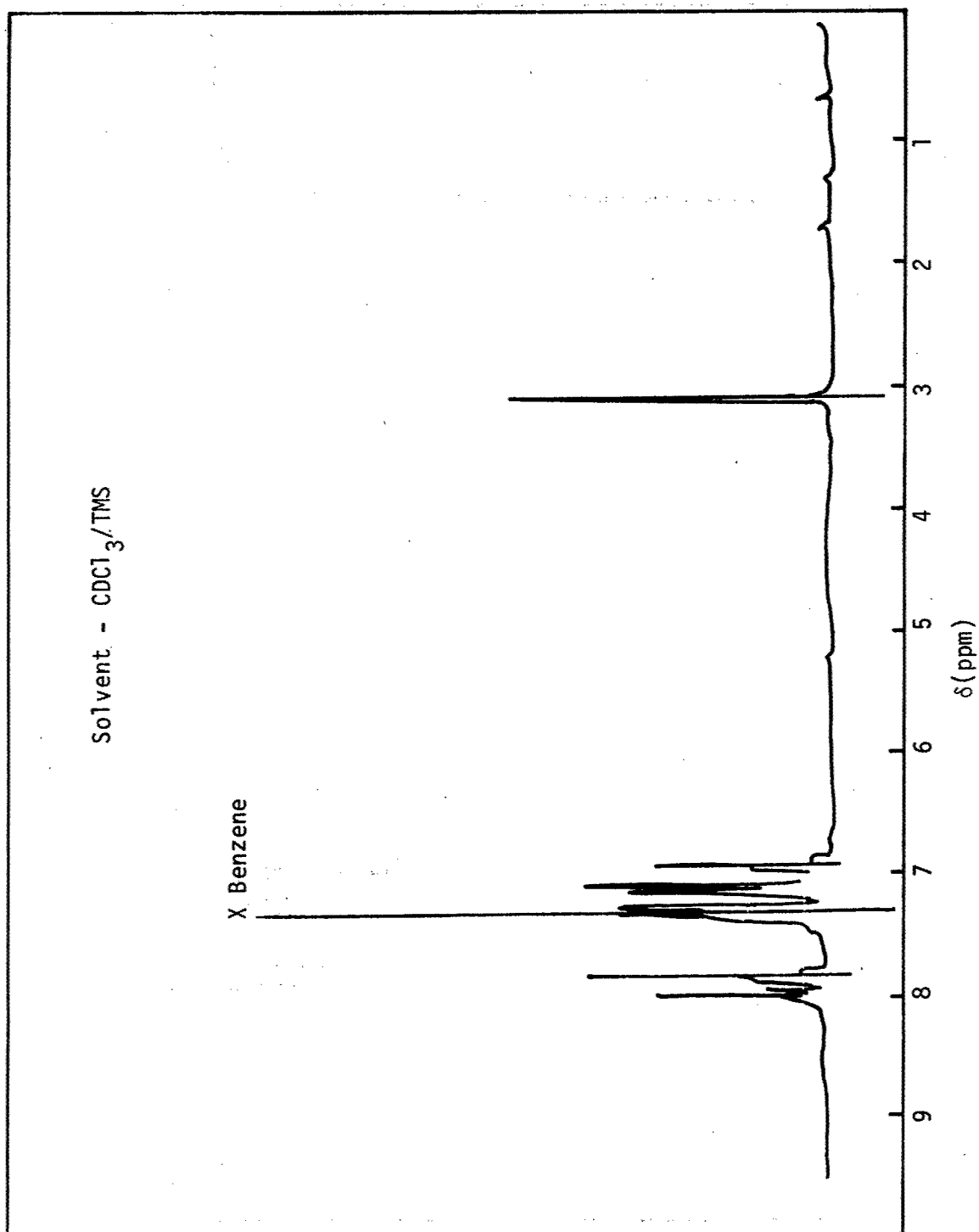


Figure 17. Proton N.M.R. Spectrum of ATS Dimer (F2)

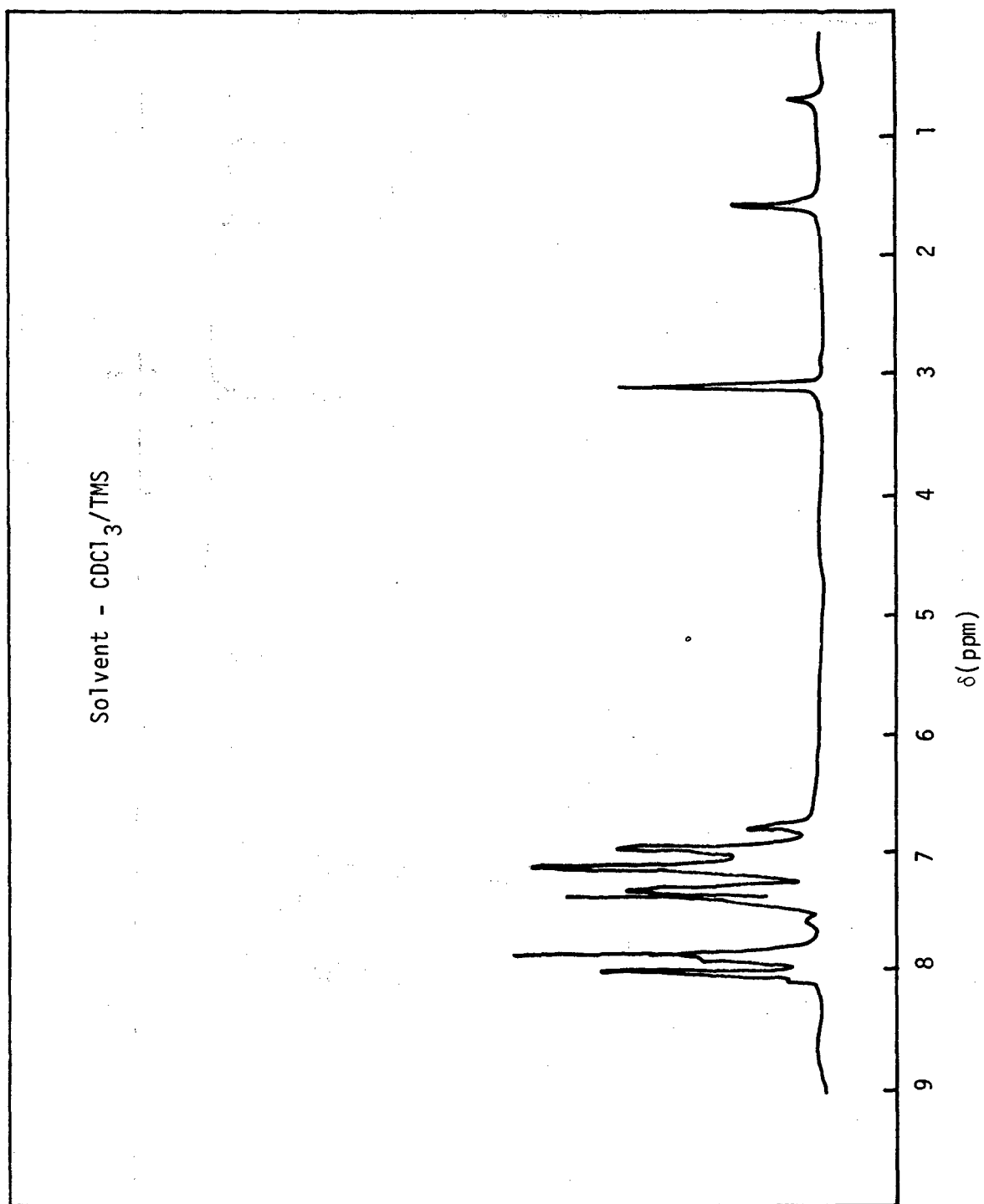


Figure 16. Proton N.M.R. Spectrum of ATS Monomer (F1)

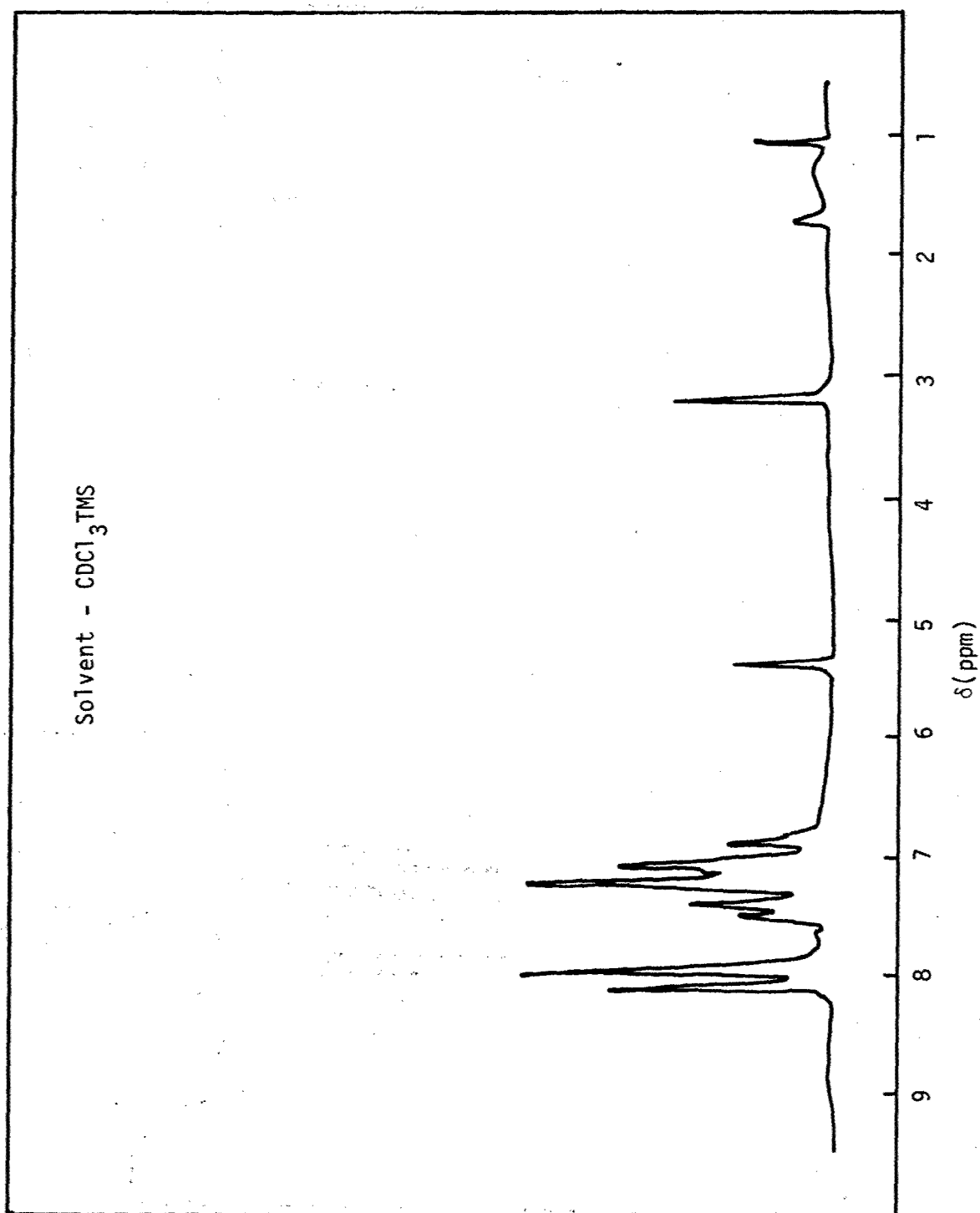


Figure 18. Proton N.M.R. Spectrum of ATS Trimer (F3)

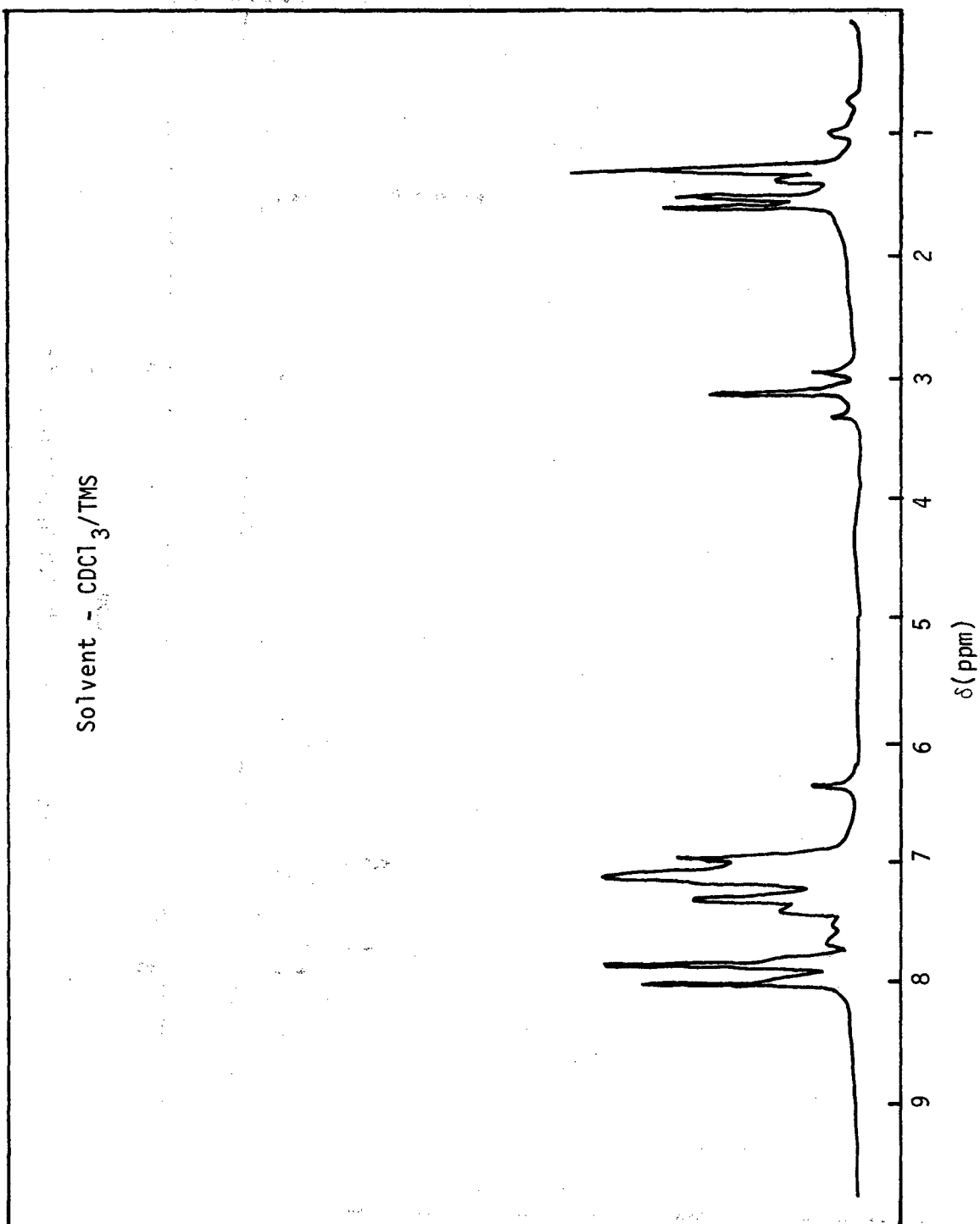


Figure 19. Proton N.M.R. Spectrum of F4

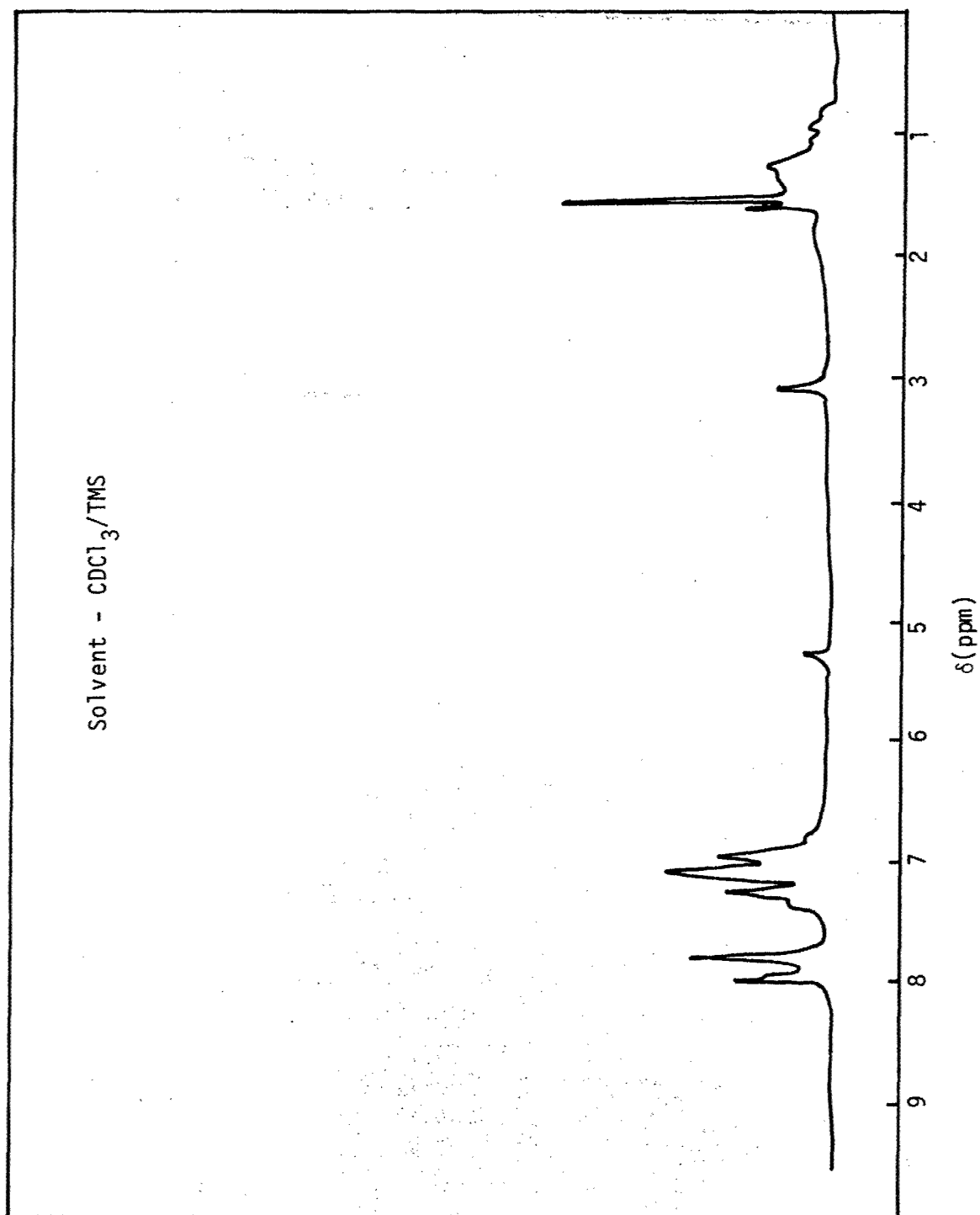


Figure 20. Proton N.M.R. Spectrum of F5

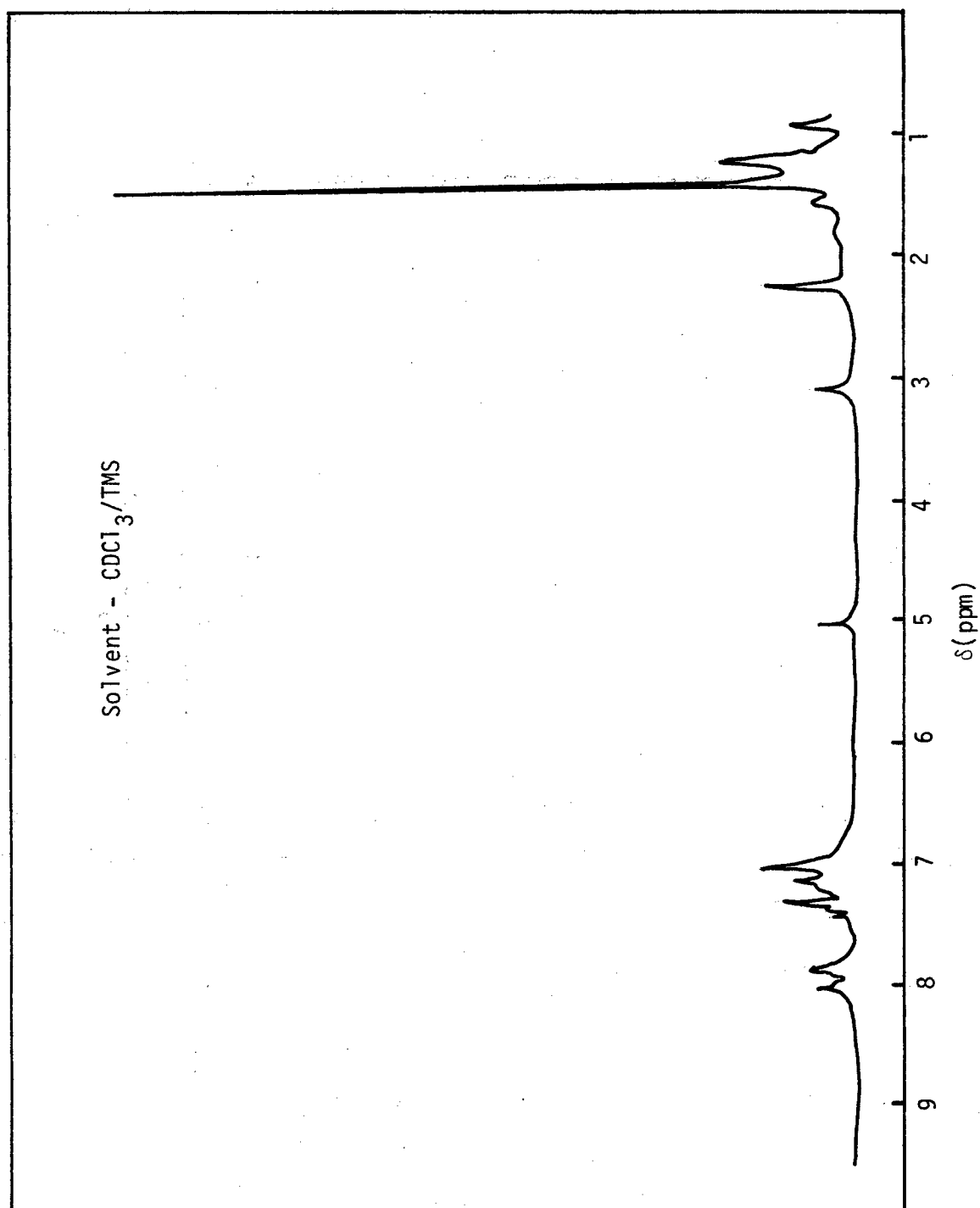


Figure 21. Proton N.M.R. Spectrum of F6

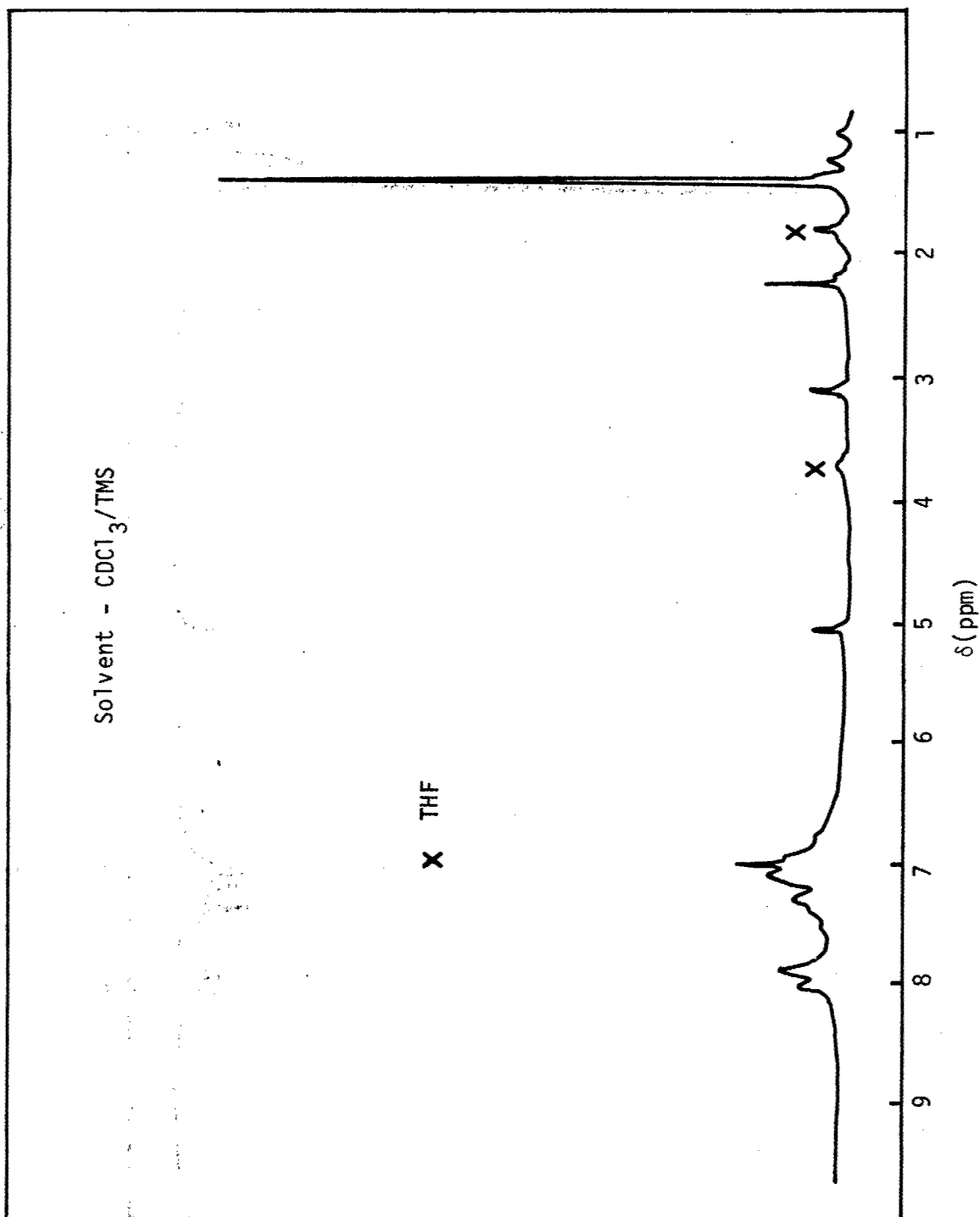


Figure 22. Proton N.M.R. Spectrum of VAA (F7)

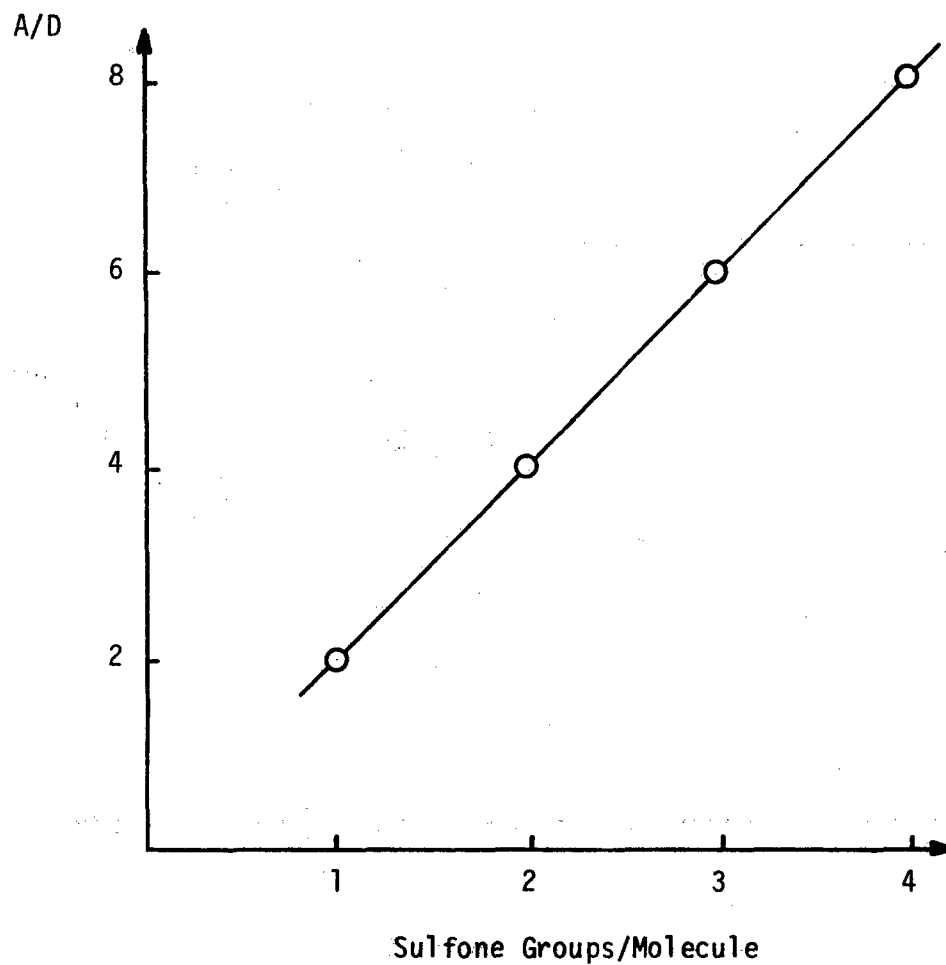


Figure 23. Relationship of A/D Proton Ratios to Sulfone Content for ATS Type Molecules

Extra Phenoxy Content

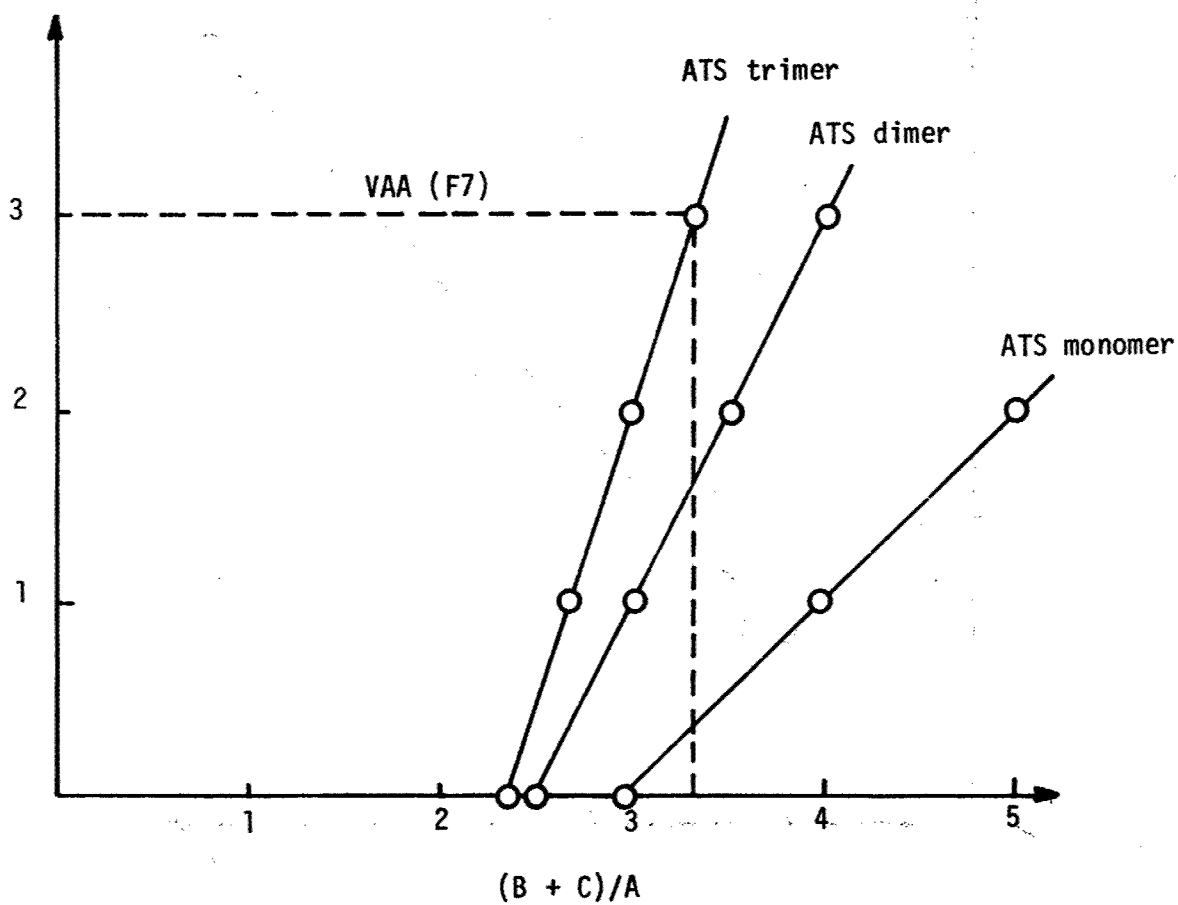


Figure 24. Relationship of  $(B + C)/A$  Proton Ratios to Extra Phenoxy Content in ATS Monomer, Dimer and Trimer

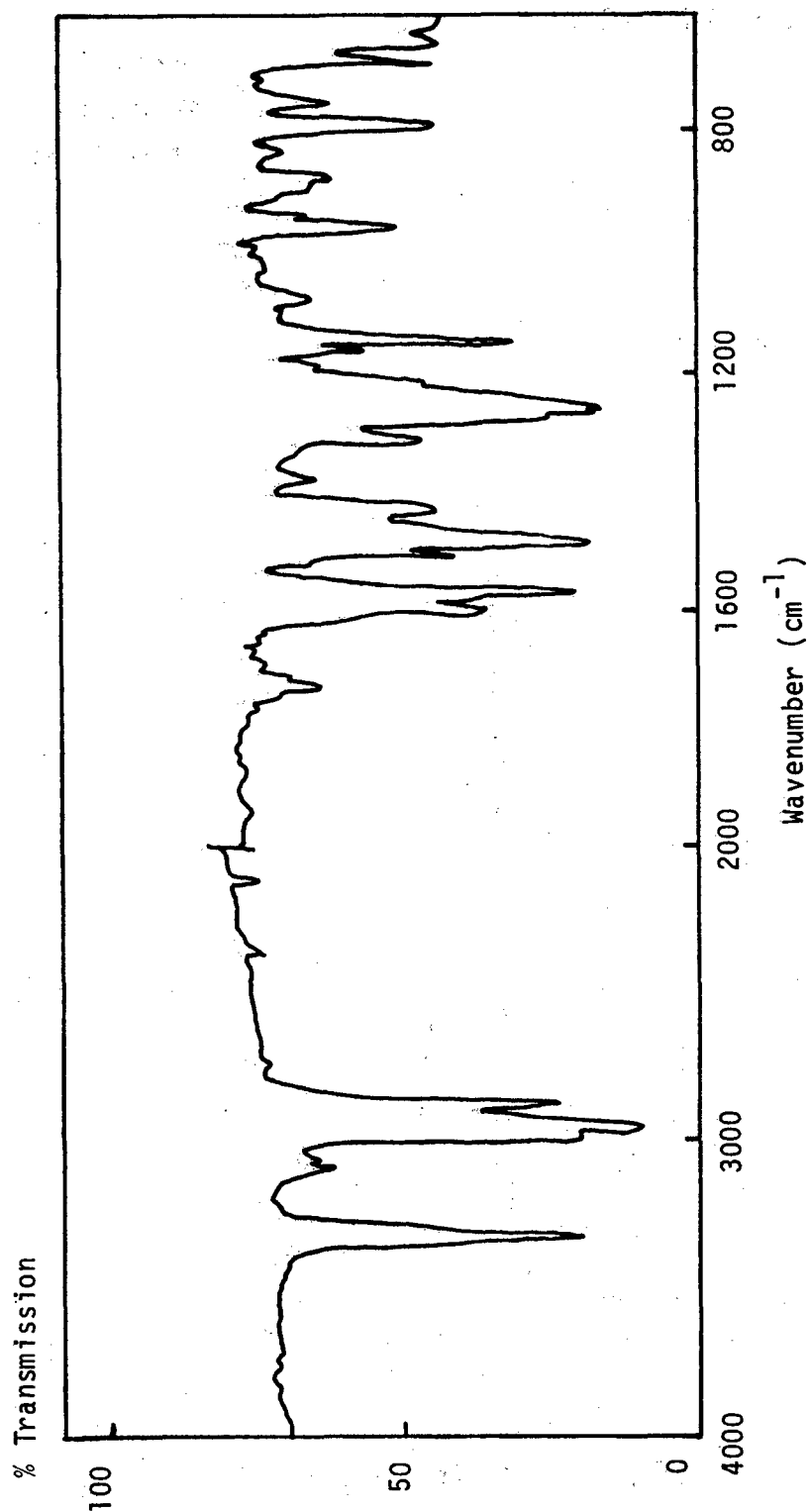


Figure 25. I.R. Spectrum of F8

Solvent THF

Flow rate 2.5 ml/min

KEY

1/

EHR 120Å

RV 40.31 ml

RT 16.12 min

U.V. Absorbance at 254 nm

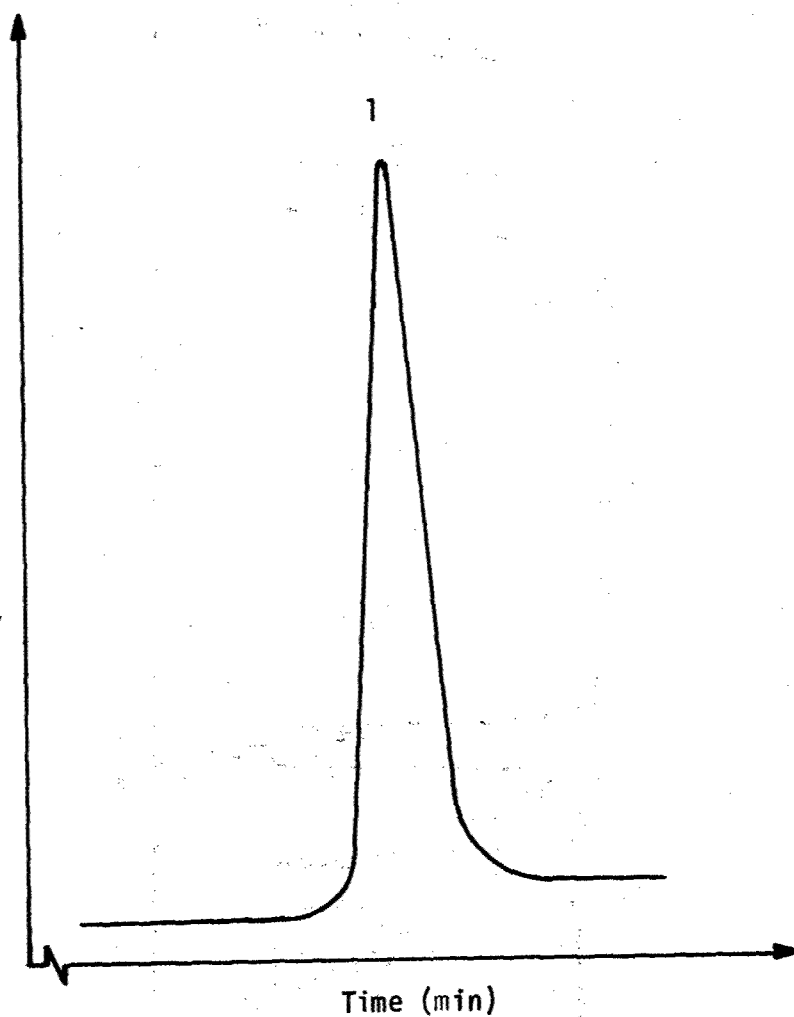


Figure 26. GPC Analysis of F8

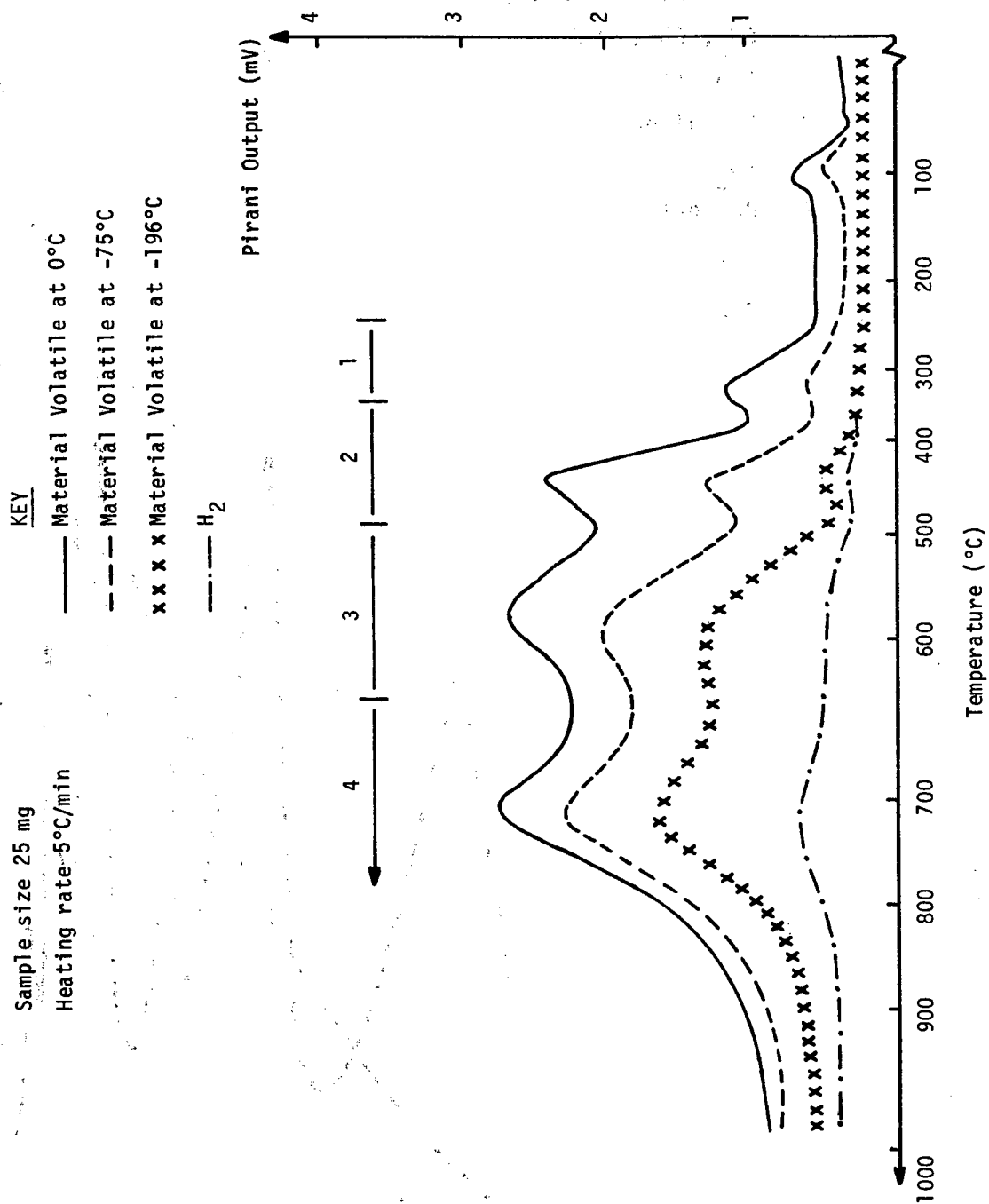


Figure 27. Thermal Volatilization Analysis (TVA) of F7

KEY

--- ( - ) Thermocouple Output (Trap Temperature)

—— Pirani Output (Pressure)

1 CO<sub>2</sub>, COS, H<sub>2</sub>S

2 Propene

3 Butadiene

4 SO<sub>2</sub>

5 Benzene

6 Water

7 Phenol

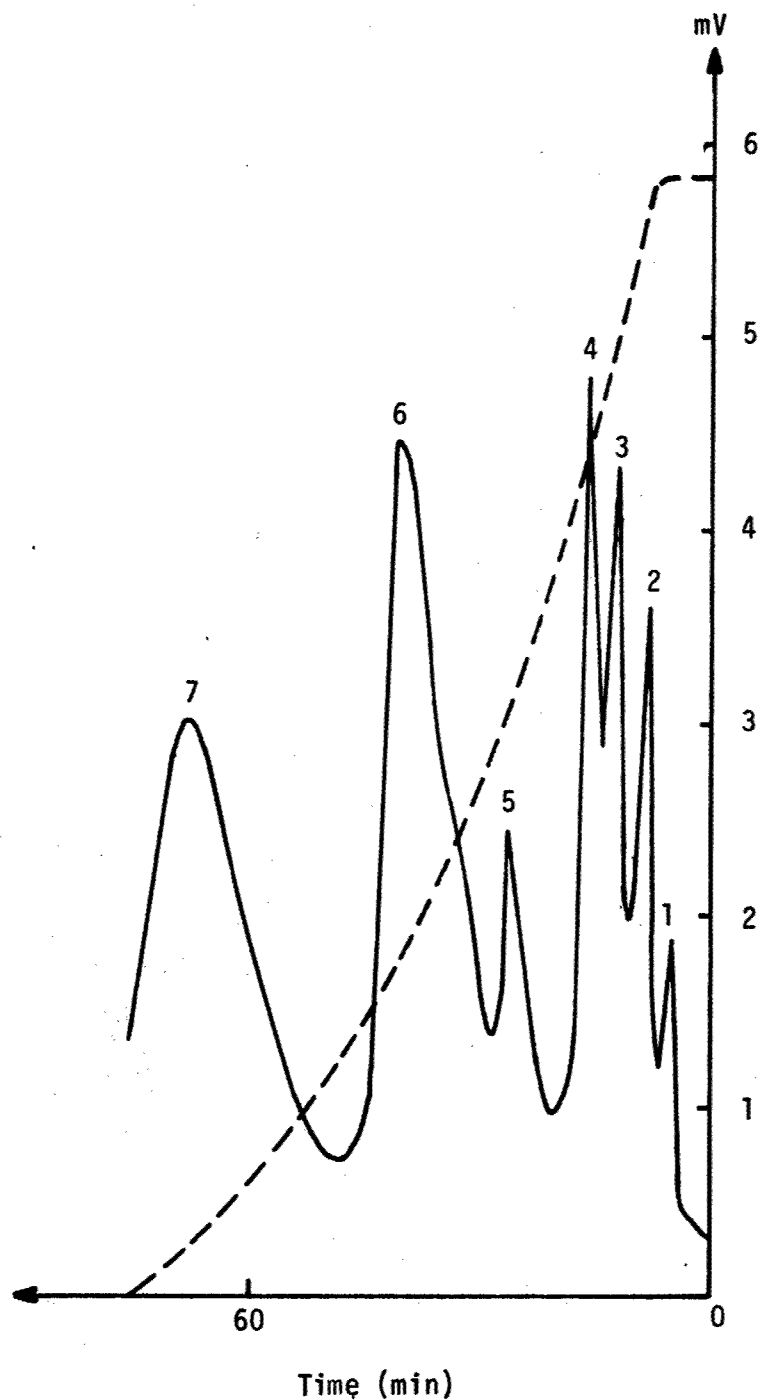


Figure 28. Sub Ambient Thermal Volatilization Analysis (SATVA) of the Condensable Volatile Products of Thermal Degradation of VAA (F7) to 1018°C

Sample size 102 mg

KEY

--- ( - ) Thermocouple Output (Trap Temperature)  
 — Pirani Output (Pressure)

- 1  $\text{CO}_2$ , COS,  $\text{H}_2\text{S}$
- 2 Propene
- 3 Butadiene
- 4  $\text{SO}_2$
- 5 Benzene
- 6 Water
- 7 Phenol

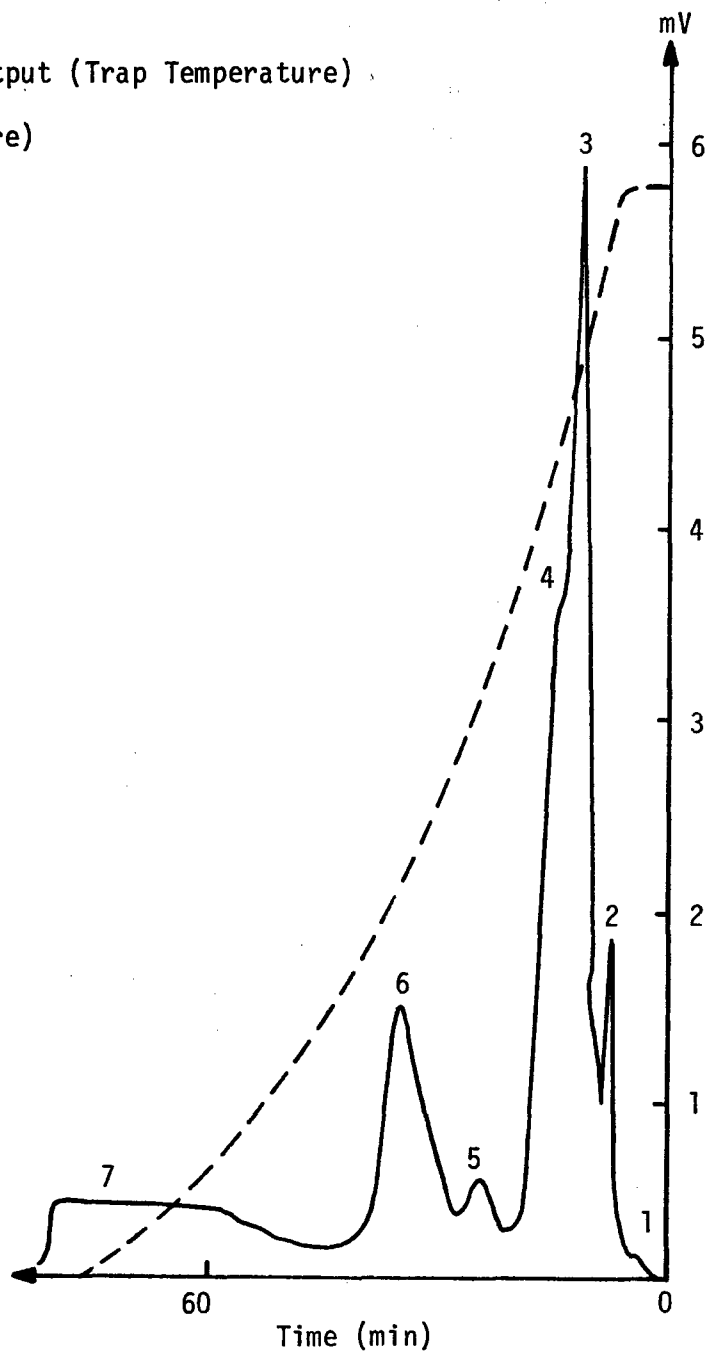


Figure 29. SATVA of the Condensable Volatile Products of Thermal Degradation of VAA (F7) in the Temperature Range (283 - 391)°C (Step 1)

Sample size 102 mg

KEY

--- ( - ) Thermocouple Output (Trap Temperature)

— Pirani Output (Pressure)

1  $\text{CO}_2$ ,  $\text{COS}$ ,  $\text{H}_2\text{S}$

2 Propene

3 Butadiene

4  $\text{SO}_2$

5 Benzene

6 Water

7 Phenol

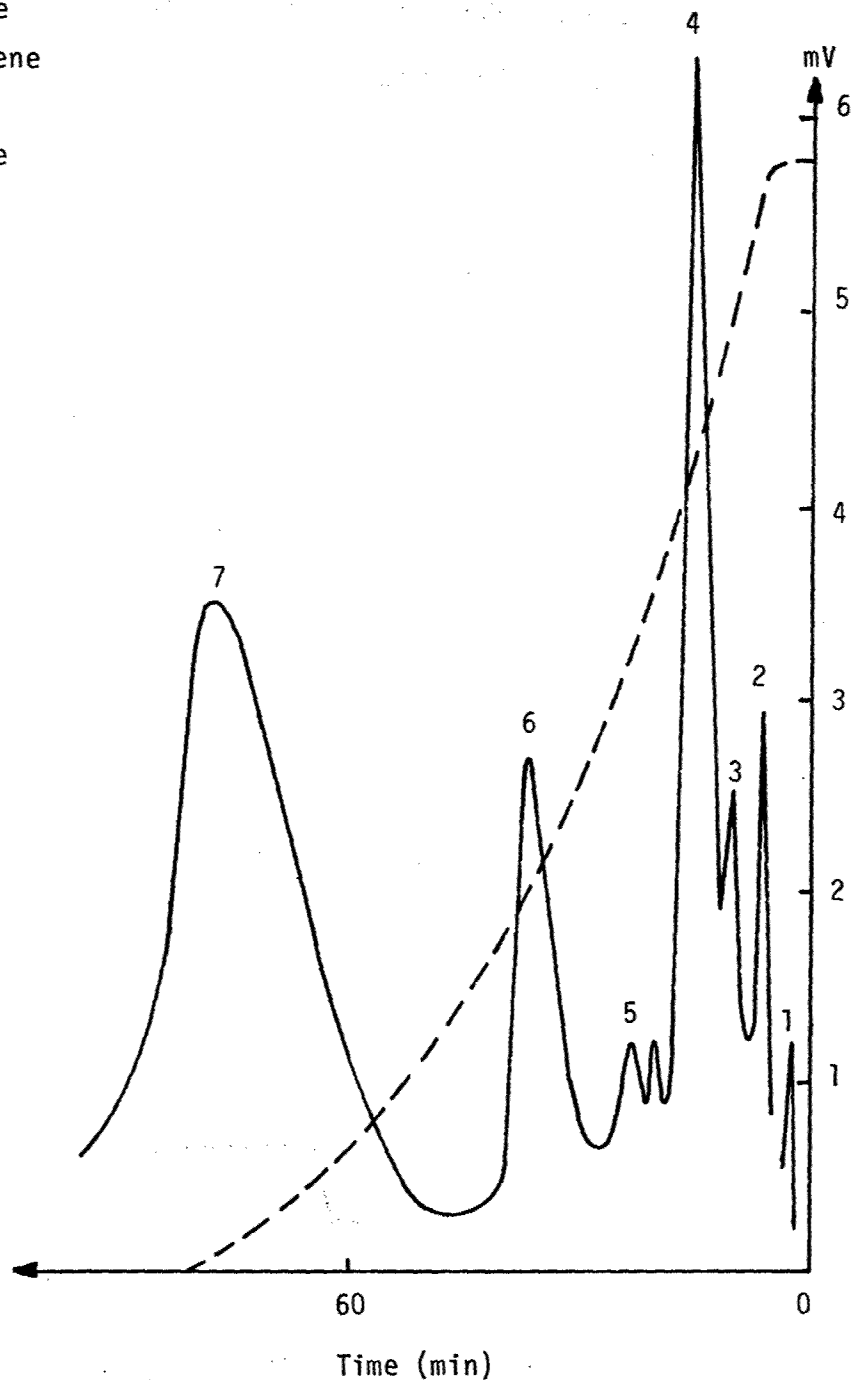


Figure 30. SATVA of the Condensable Volatile Products of Thermal Degradation of VAA (F7) in the Temperature Range (391 - 526)°C (Step 2)

Sample size 102 mg

KEY

--- ( - ) Thermocouple Output (Trap Temperature)

— Pirani Output (Pressure)

1 CO<sub>2</sub>, COS, H<sub>2</sub>S

2 Propene

3 Butadiene

4 SO<sub>2</sub>

5 Benzene

6 Water

7 Phenol

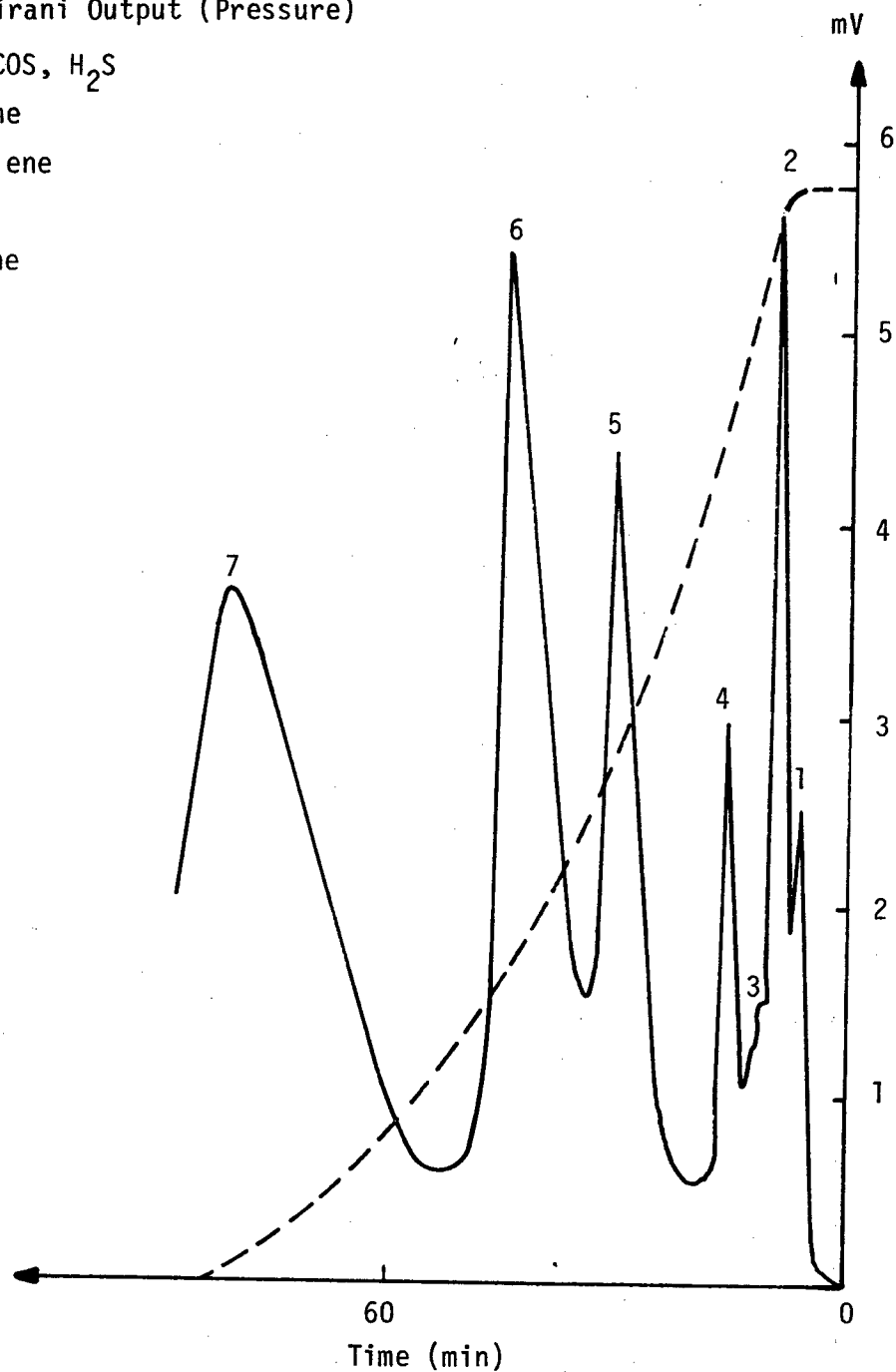


Figure 31. SATVA of the Condensable Volatile Products of Thermal Degradation of VAA (F7) in the Temperature Range (526 - 661)°C (Step 3)

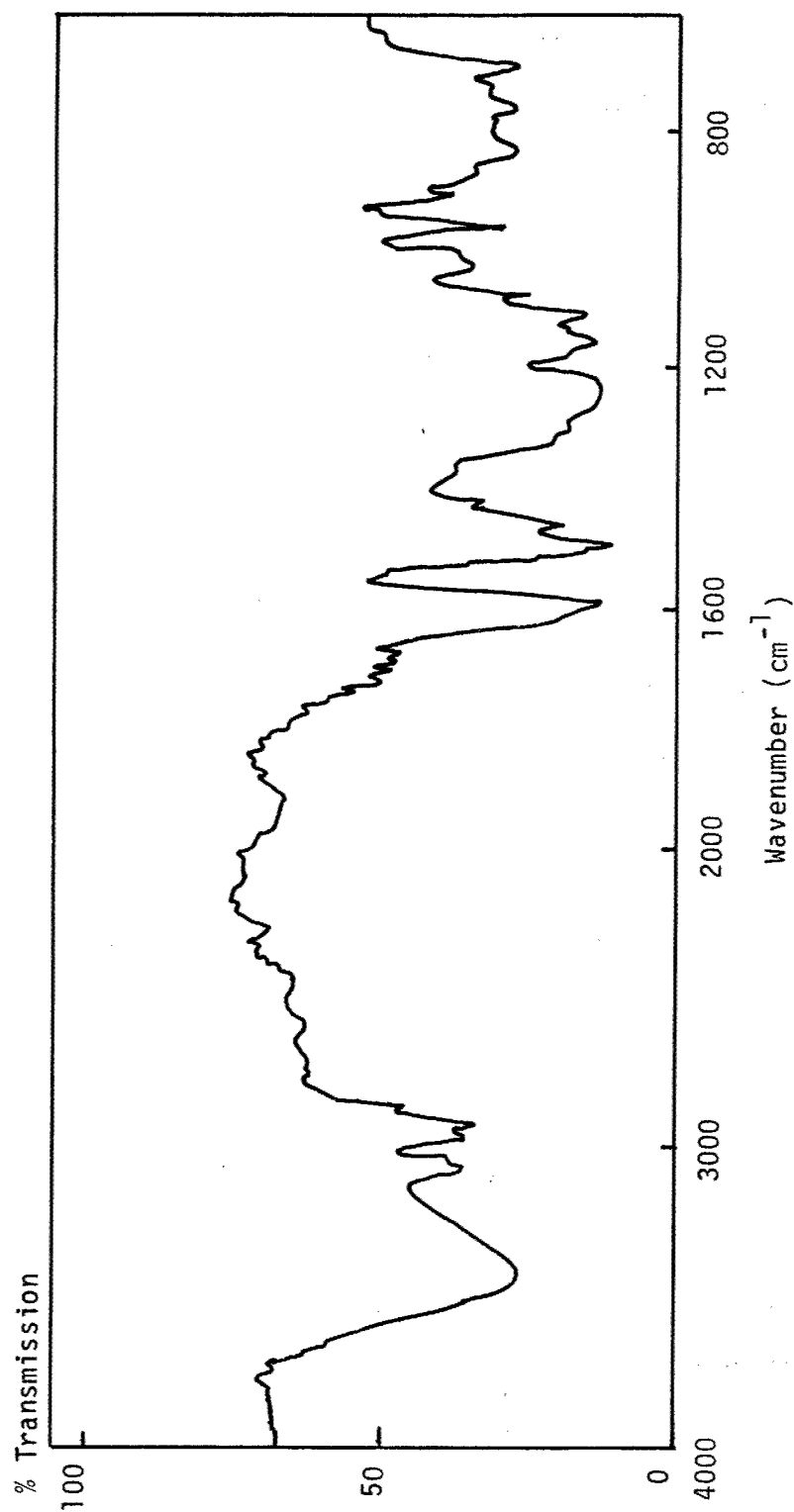


Figure 32. I.R. Spectrum of the Oligomeric Product Fraction of Thermal Degradation of VAA (F7) to 1018°C

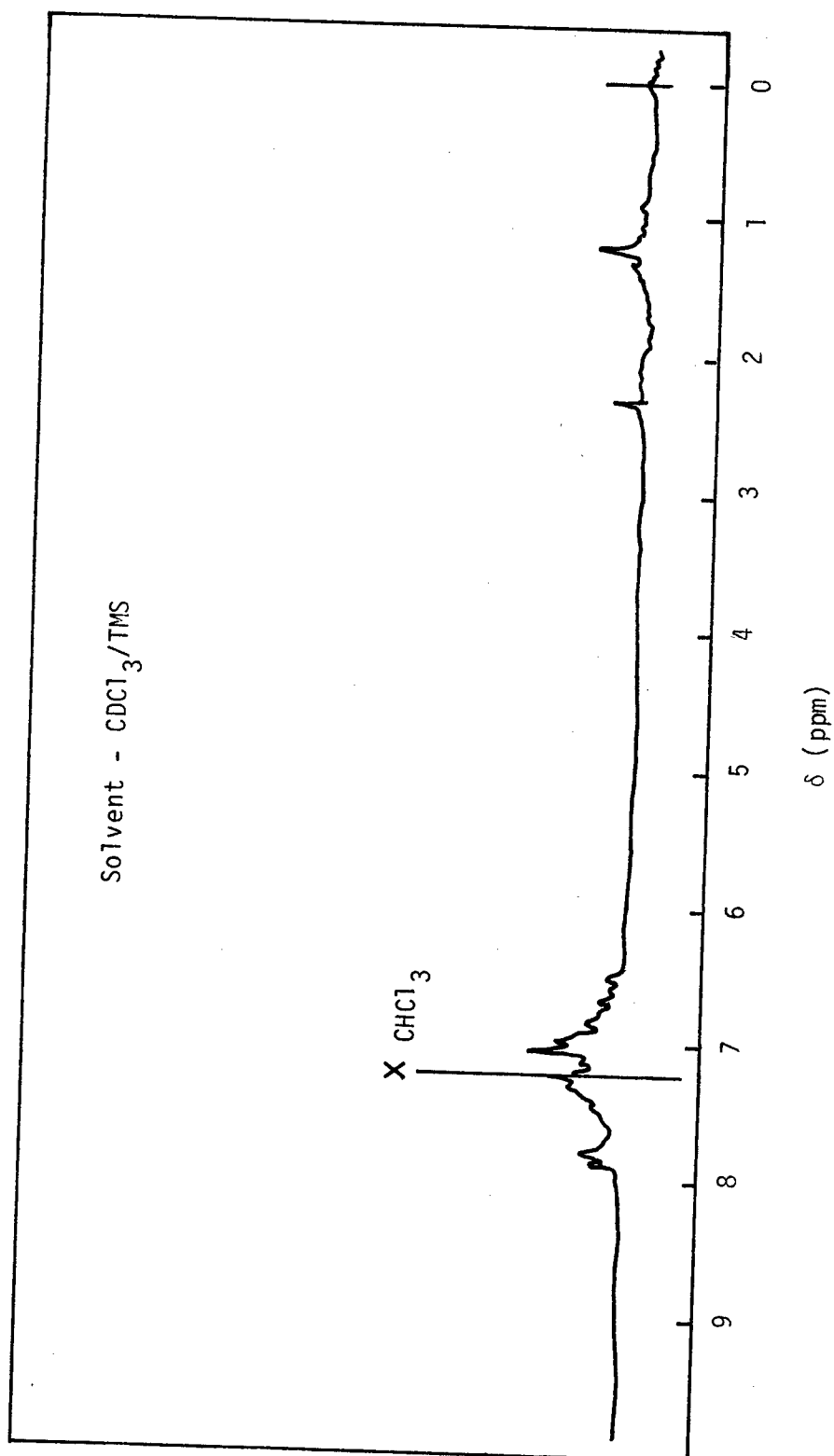


Figure 33. Proton N.M.R. Spectrum of the Oligomeric Product Fraction of Thermal Degradation of VAA (F7) to 1018°C

Atmosphere N<sub>2</sub>  
 Heating rate 10°C/min  
 Sample size 6.0 mg

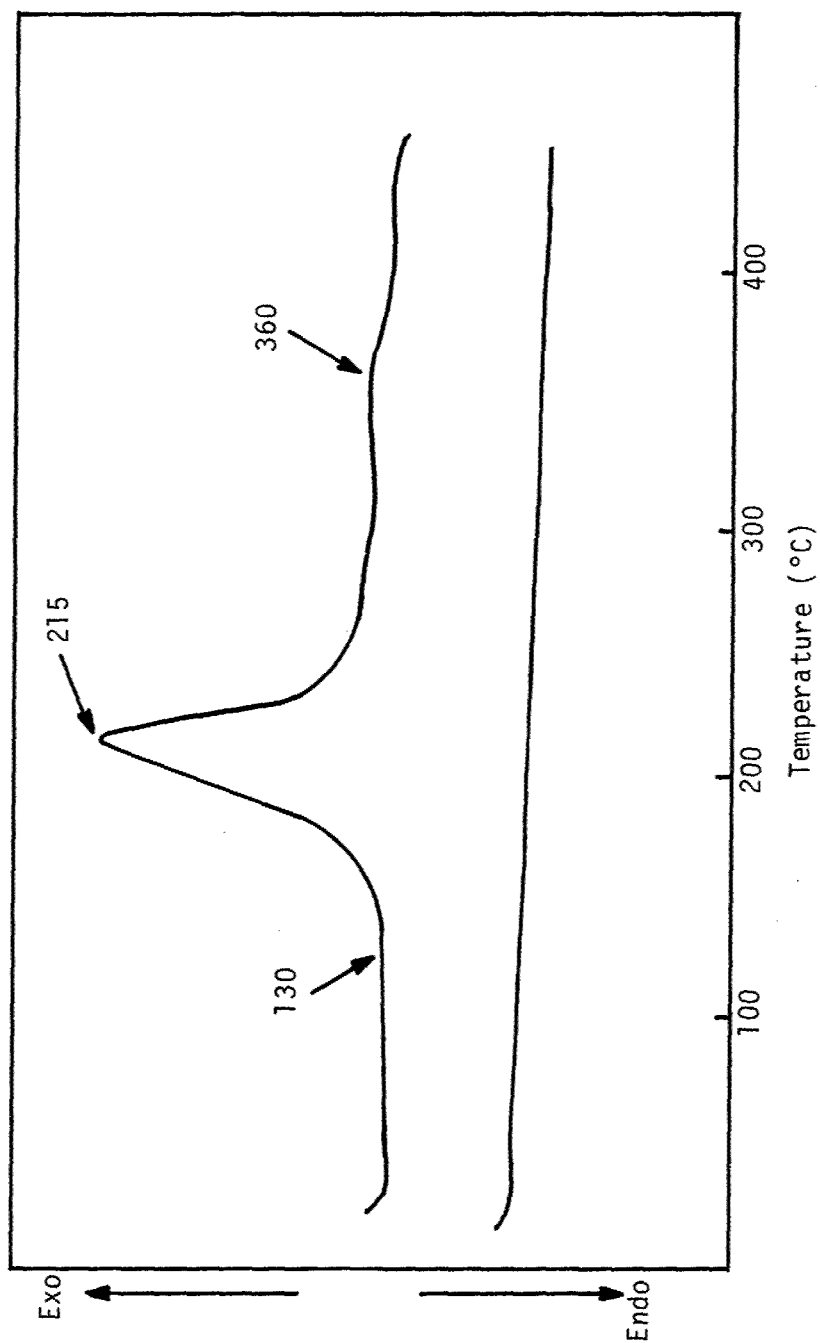


Figure 34. DSC of ATS-G

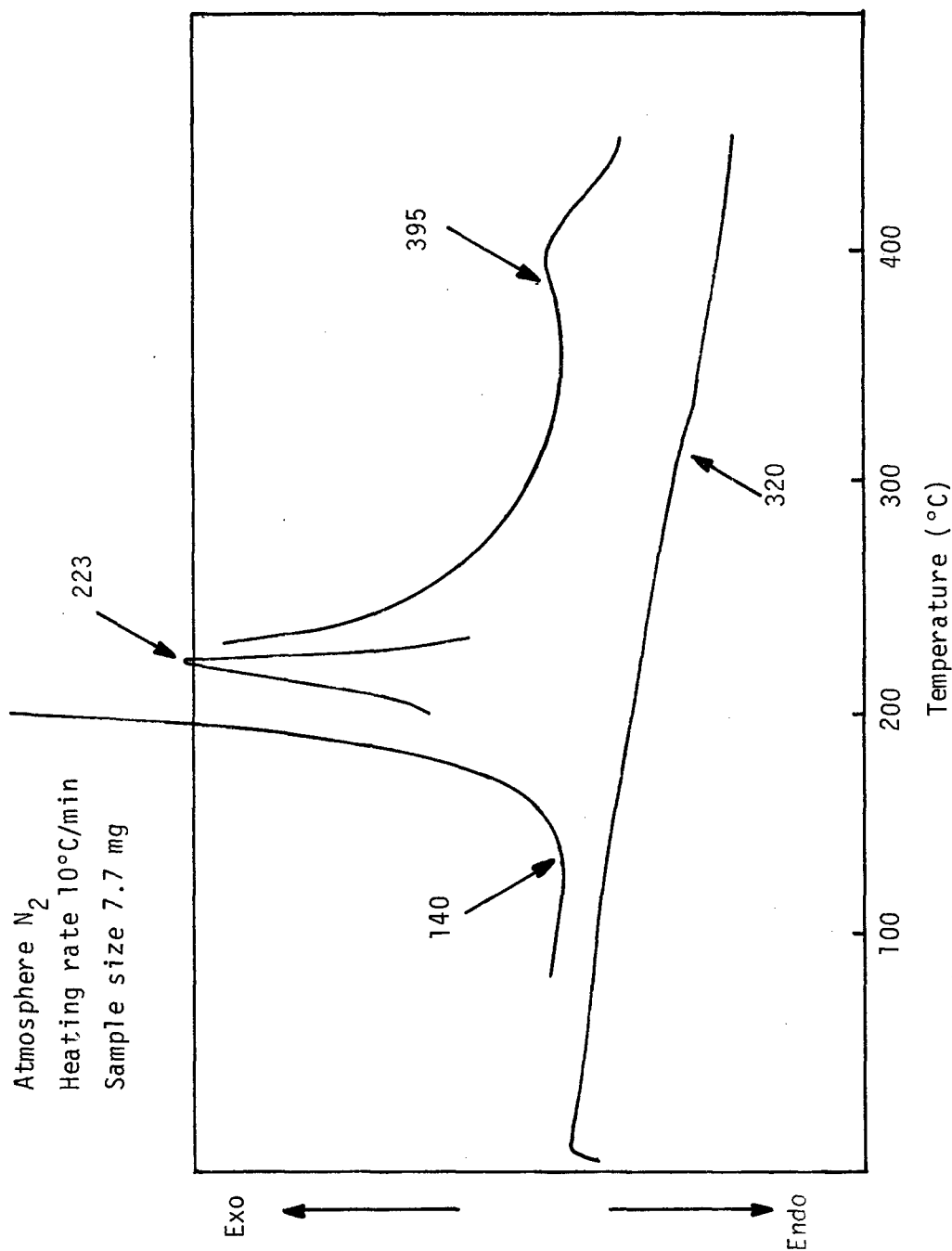


Figure 35. DSC of ATS Monomer (F1)

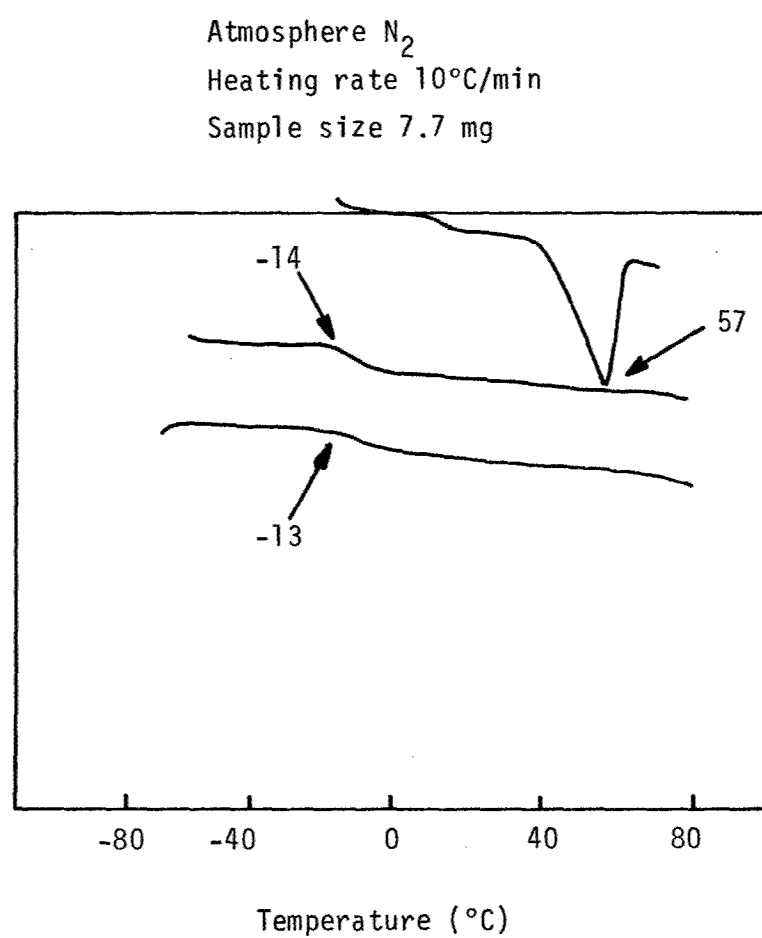


Figure 36. Subambient DSC of ATS Monomer (F1)

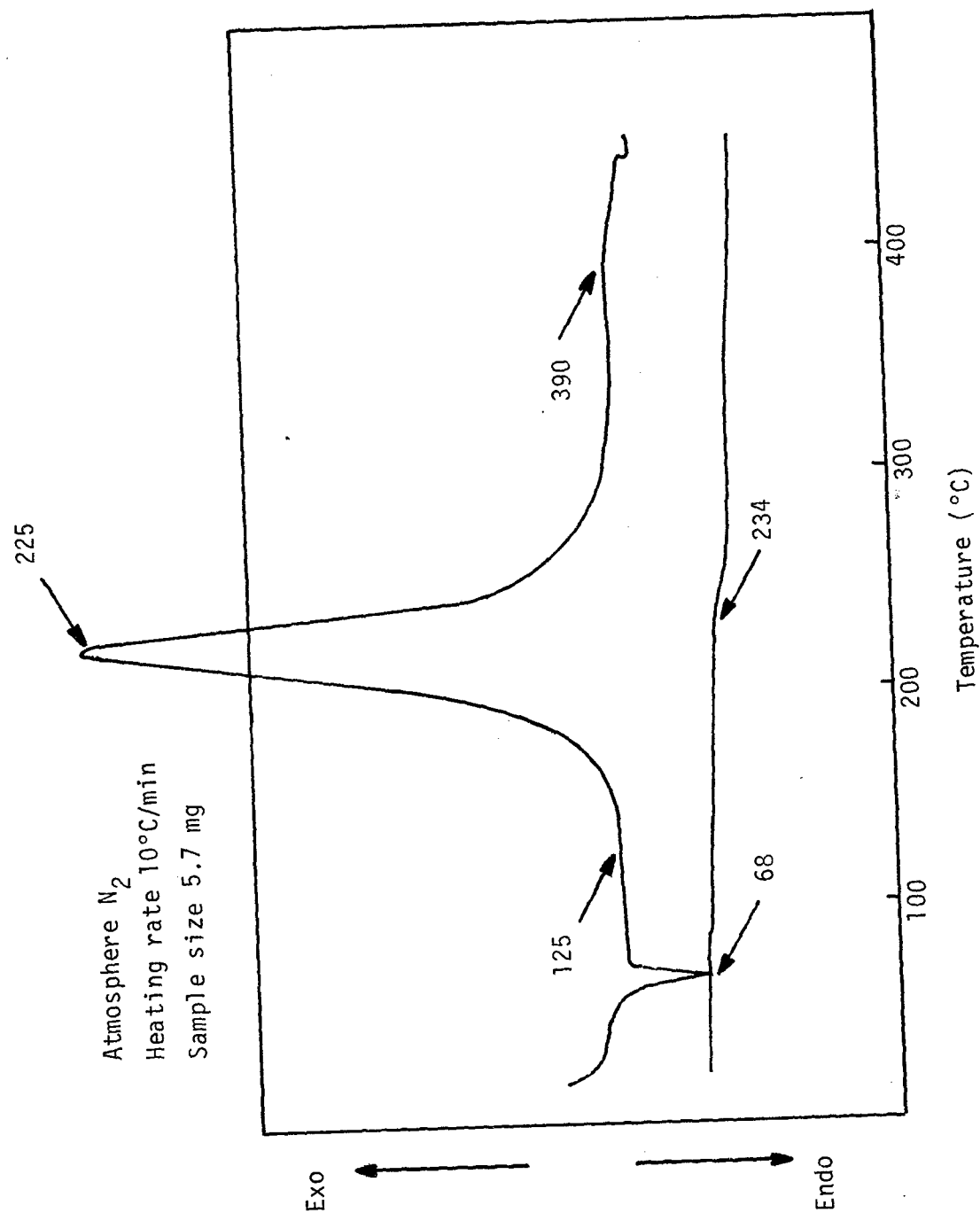


Figure 37. DSC of ATS Dimer (F2)

Atmosphere  $N_2$   
Heating rate  $10^\circ C/min$   
Sample size 4.4 mg

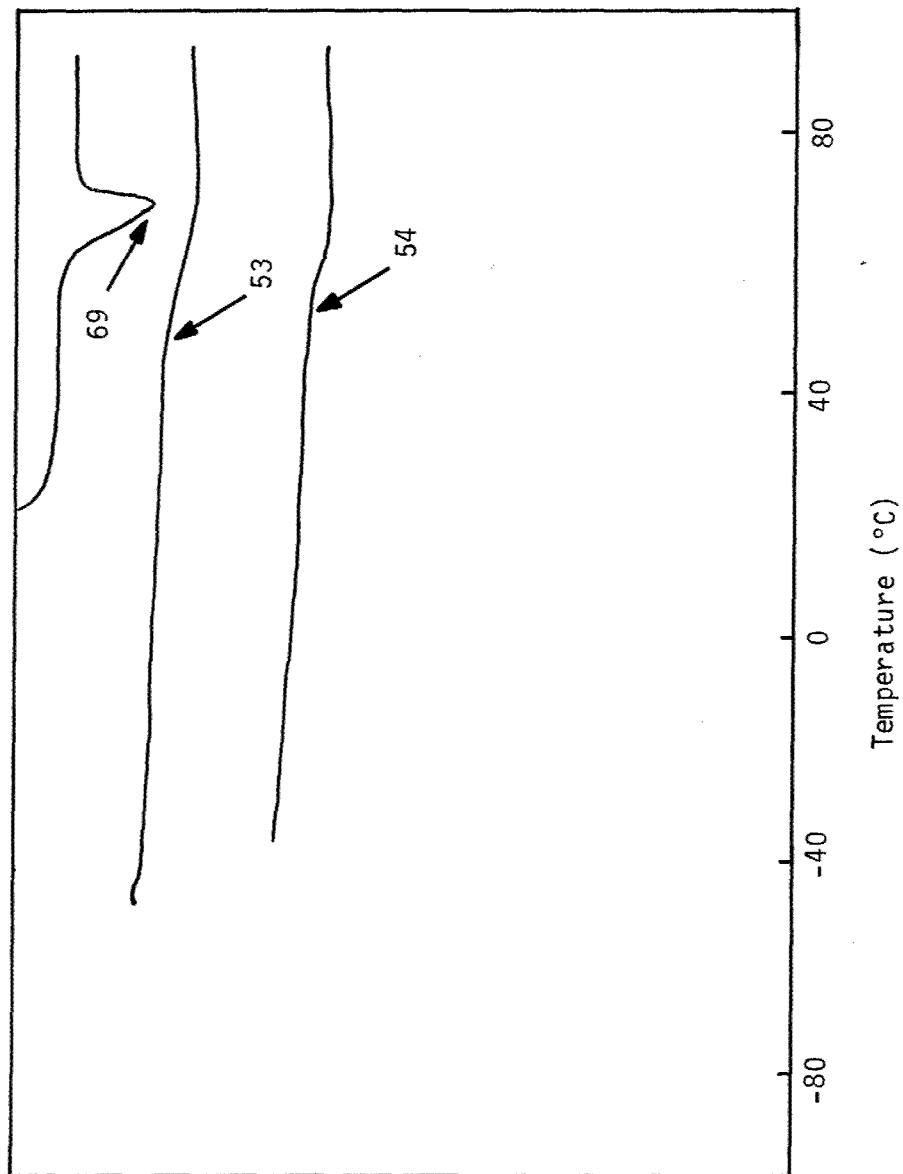


Figure 38. Subambient DSC of ATS Dimer (F2)

Atmosphere N<sub>2</sub>  
 Heating rate 10°C/min  
 Sample size 5.8 mg

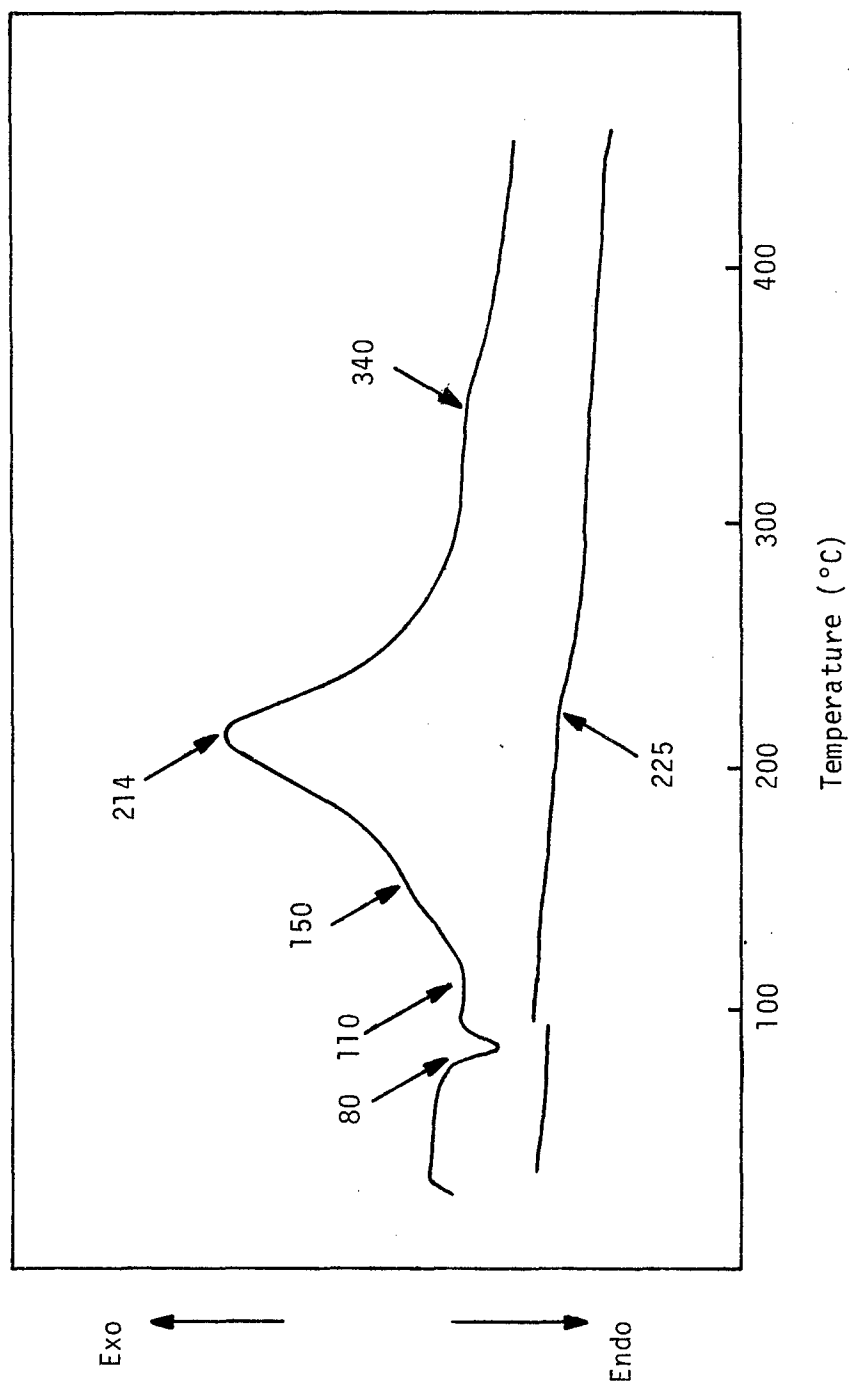


Figure 39. DSC of ATS Trimer (F3)

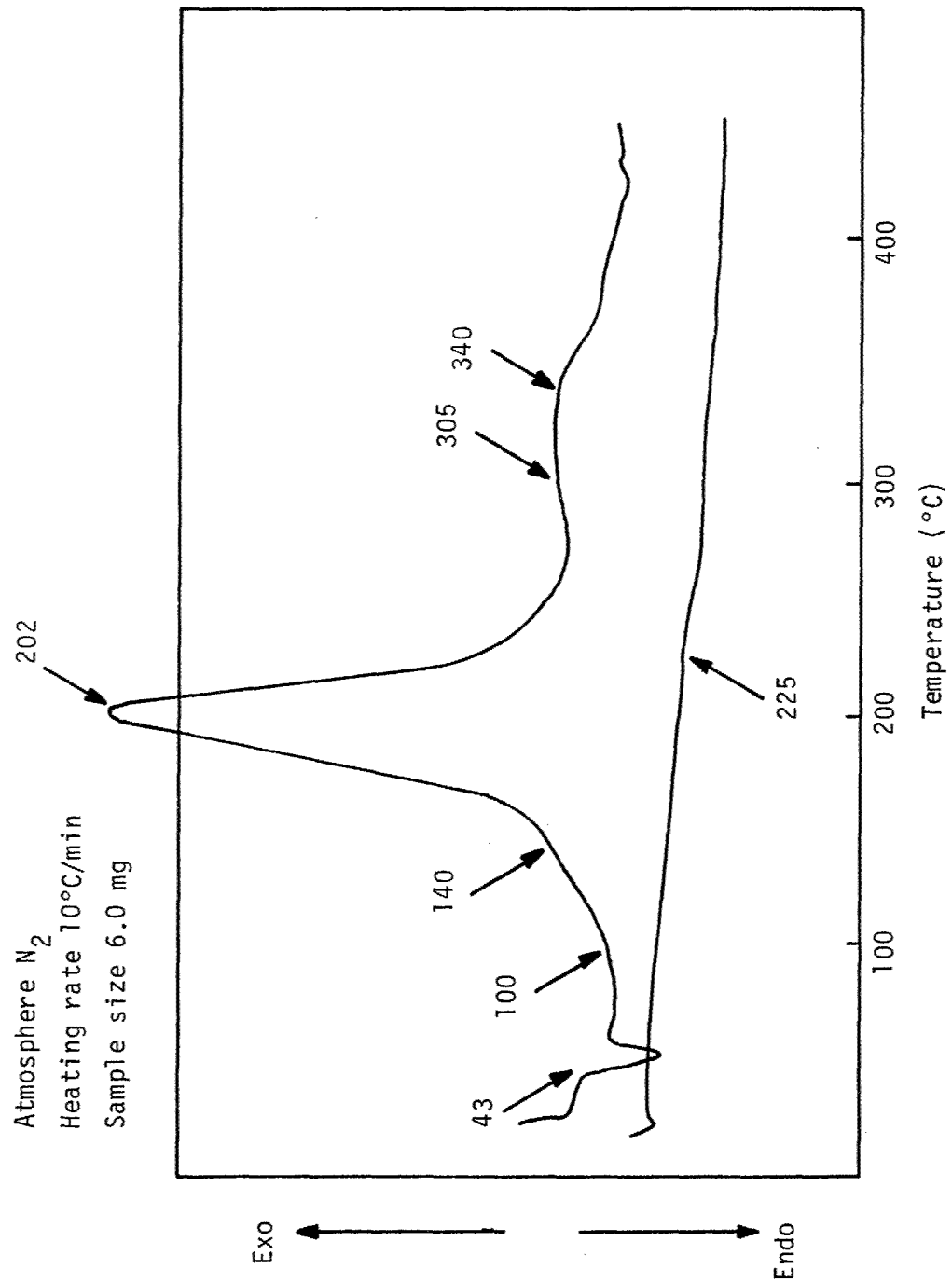


Figure 40. DSC of F4

Atmosphere N<sub>2</sub>  
 Heating rate 10°C/min  
 Sample size 6.8 mg

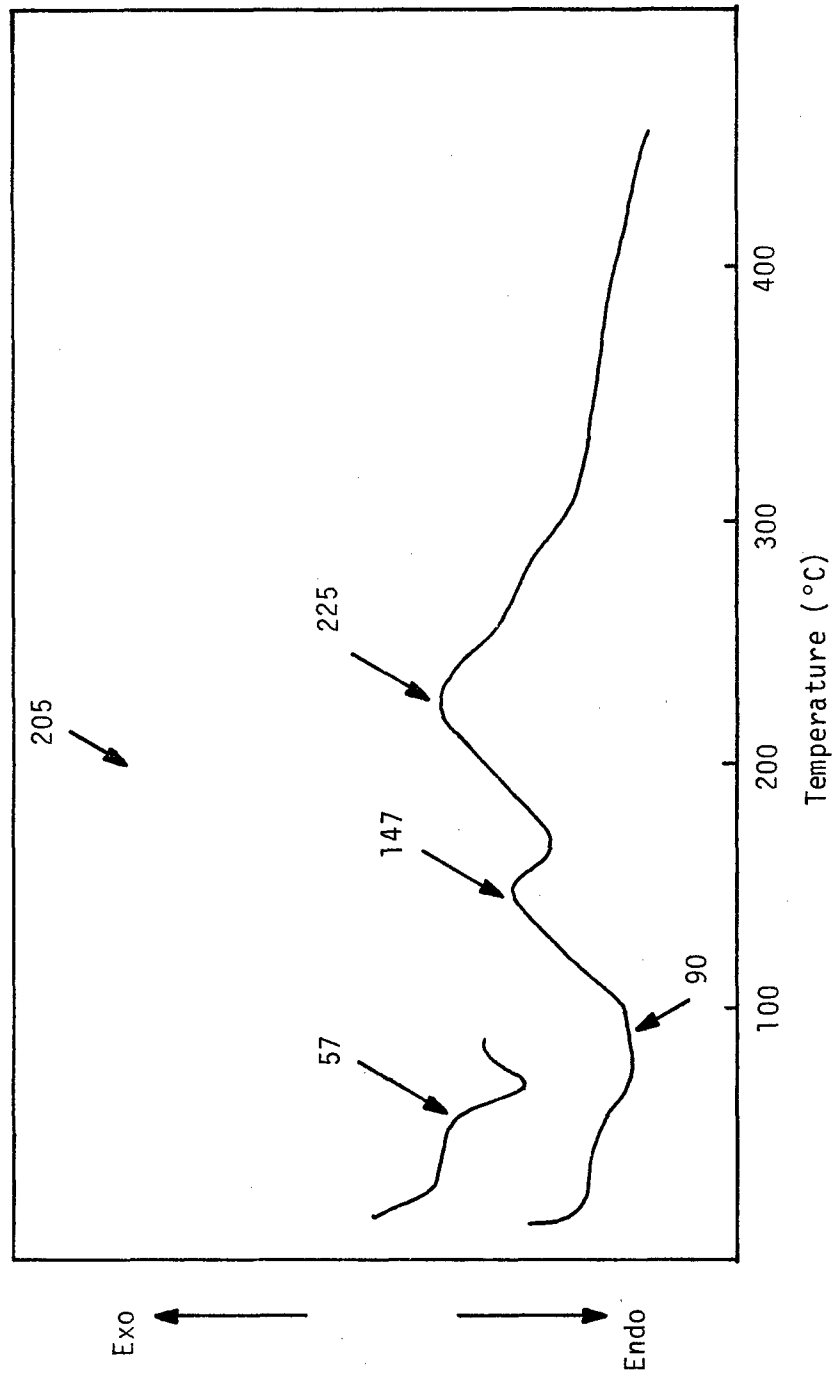


Figure 41. DSC of F5

Atmosphere N<sub>2</sub>  
Heating rate 10°C/min  
Sample size 11.8 mg

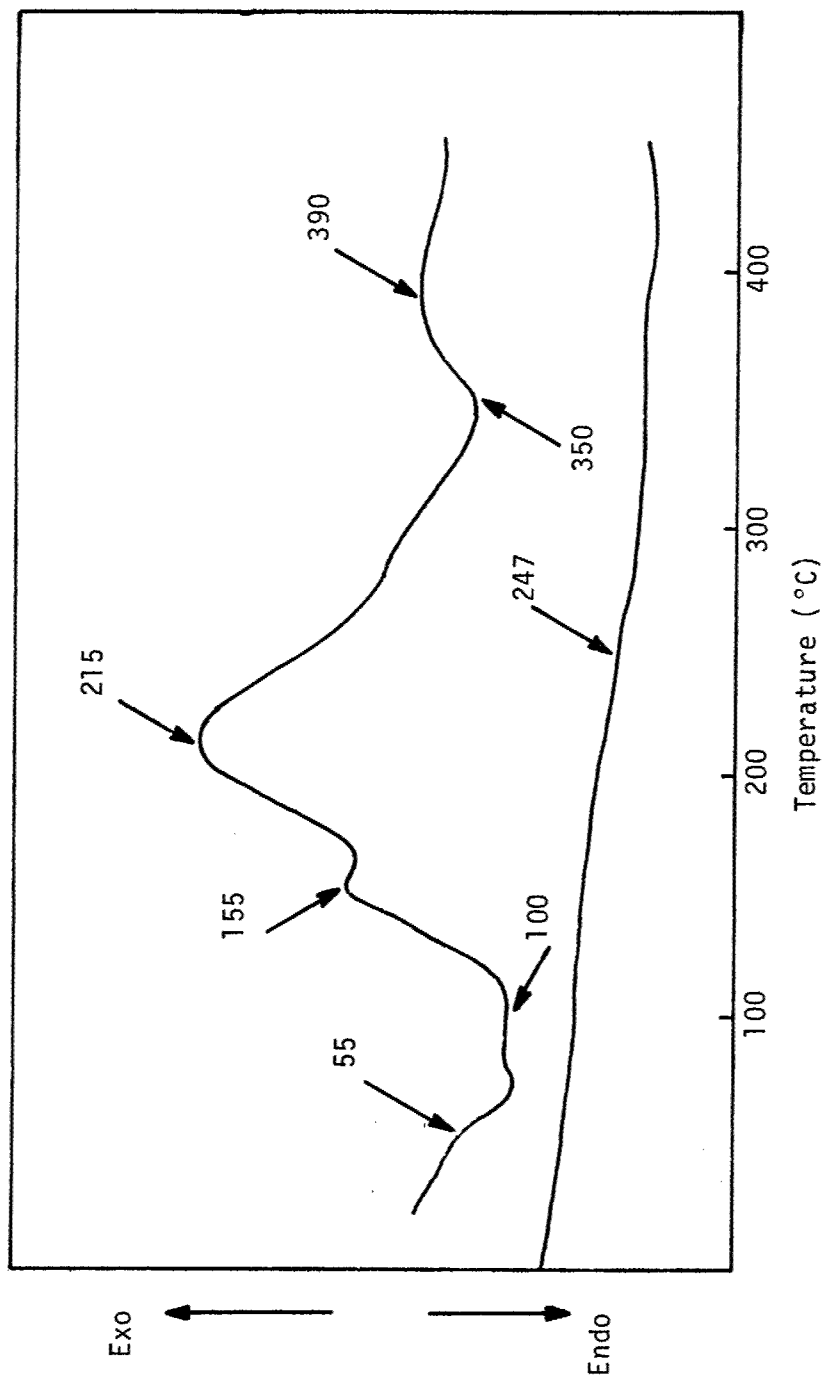


Figure 42. DSC of VAA (F7)

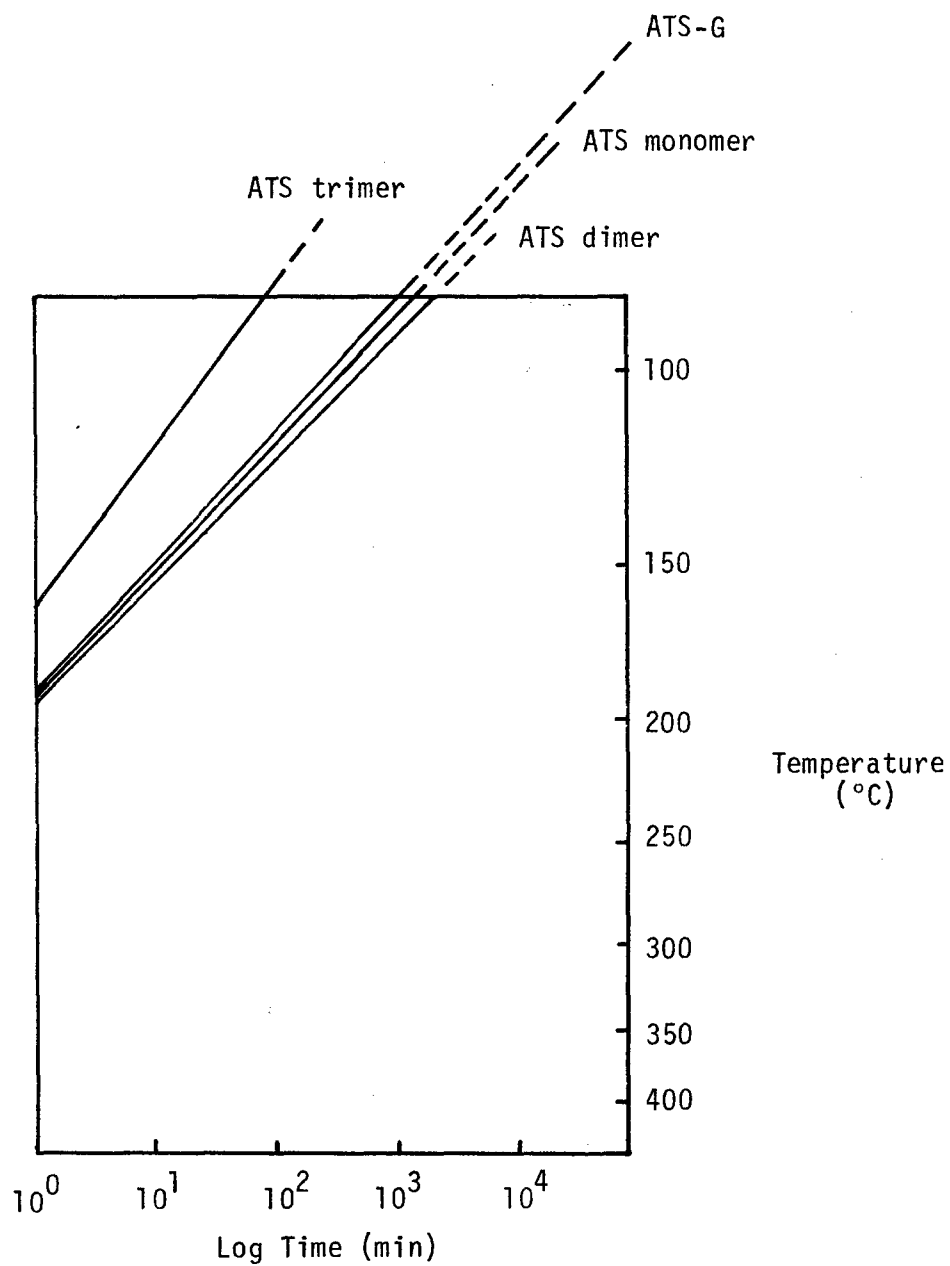


Figure 43. Reaction Window Plots for 5 Percent Conversion to Polymer

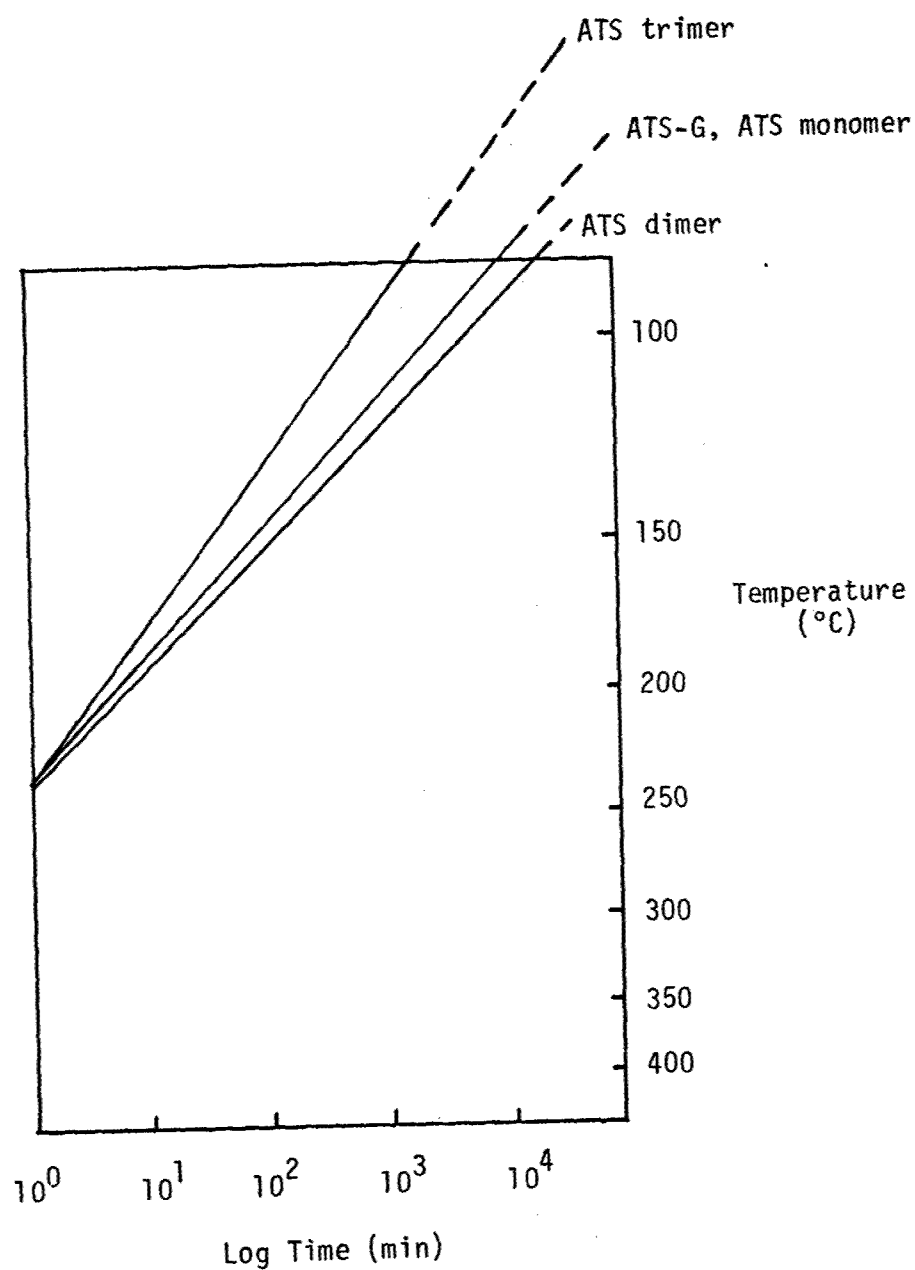


Figure 44. Reaction Window Plots for 50 Percent Conversion to Polymer

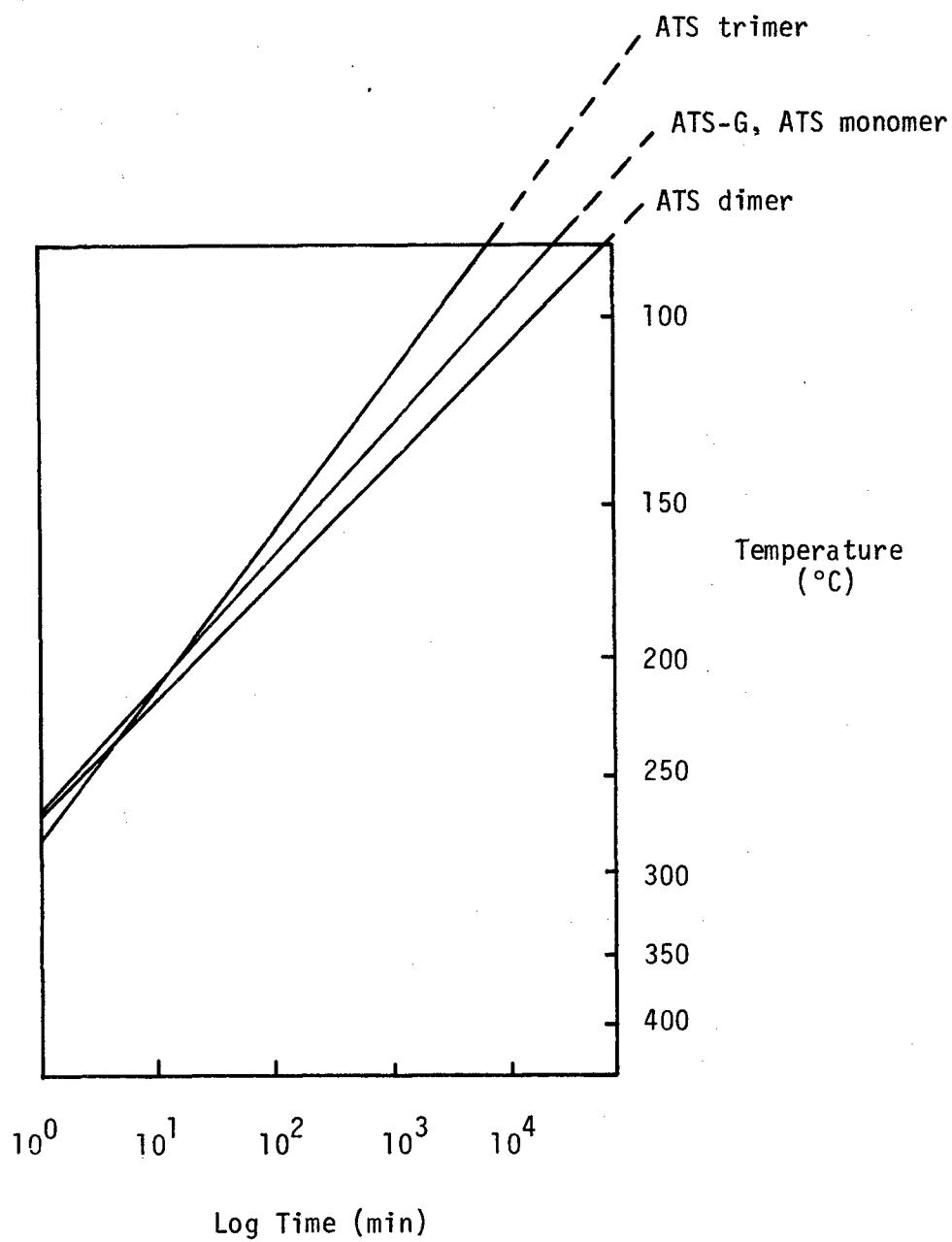


Figure 45. Reaction Window Plots for 95 Percent Conversion to Polymer

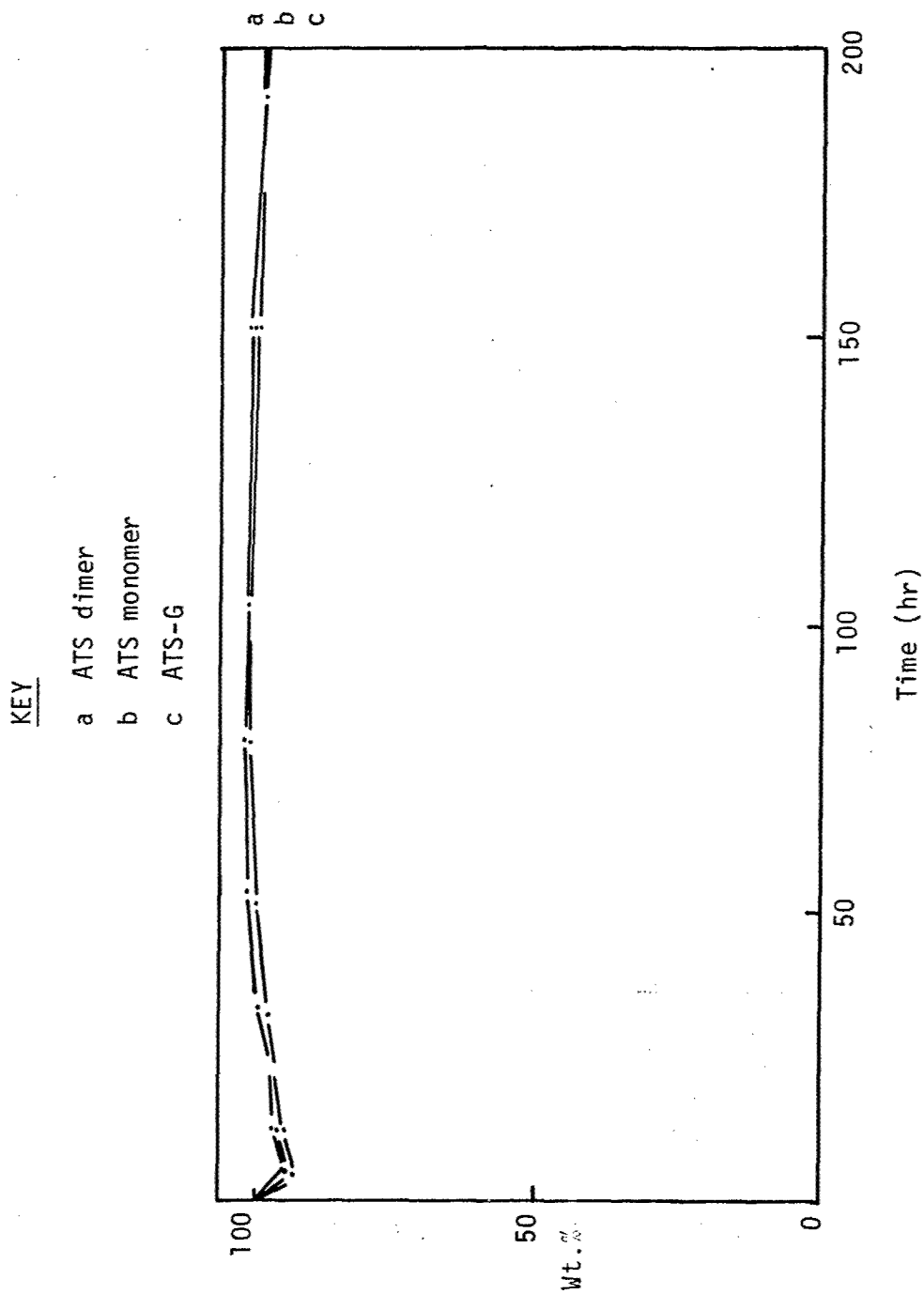


Figure 46. Isothermal Weight Losses at 260°C From ATS-G, ATS Monomer and ATS Dimer in Air

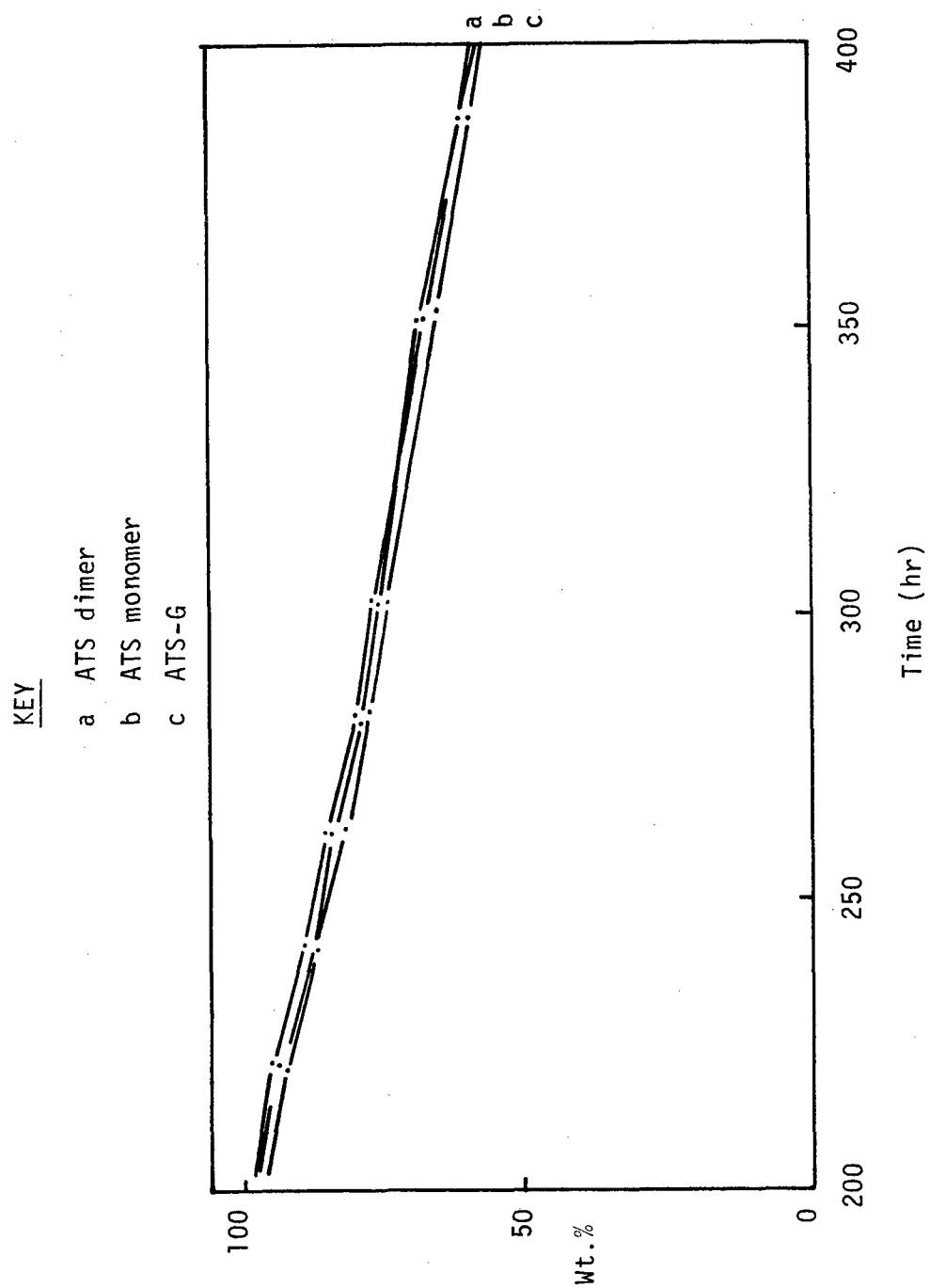


Figure 47. Isothermal Weight Losses at 316°C From ATS-G, ATS Monomer and ATS Dimer in Air

Heating rate 5°C/min  
Sample size 10.60 mg

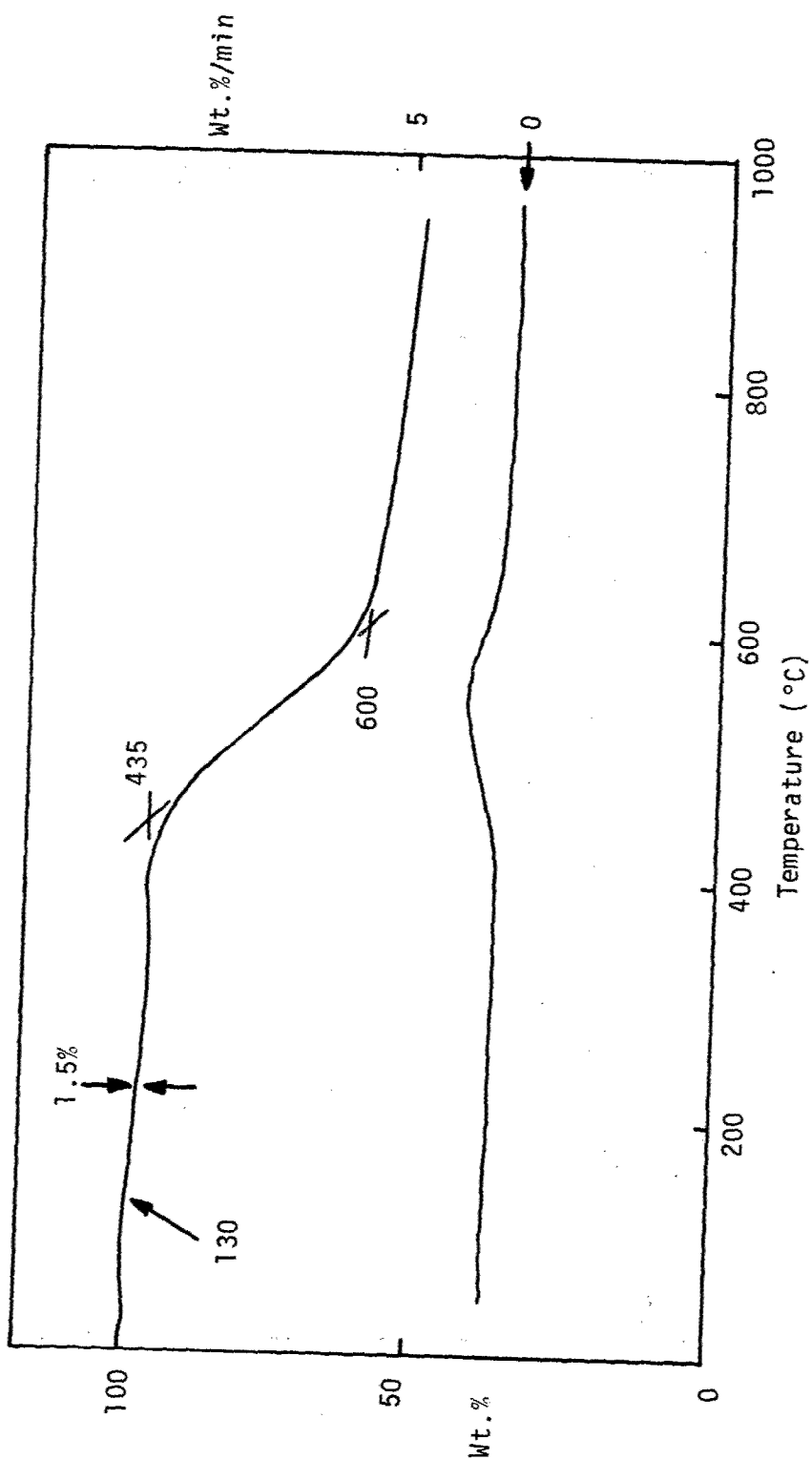


Figure 48. Programmed TGA of ATS-G Under Helium

Heating rate 5°C/min  
Sample size 12.15 mg

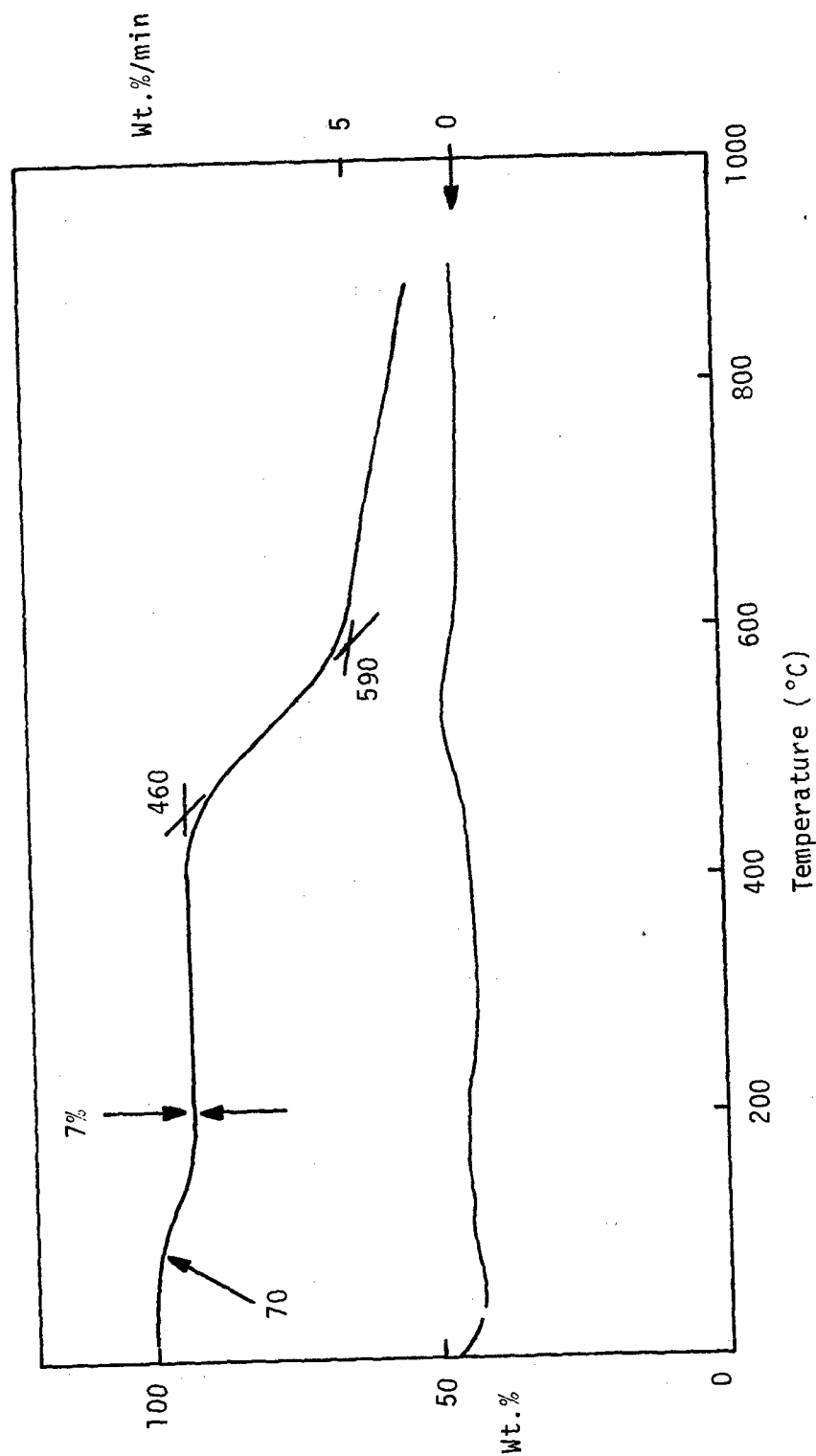


Figure 49. Programmed TGA of ATS Monomer (F1) Under Helium

Heating rate 5°C/min  
Sample size 12.00 mg

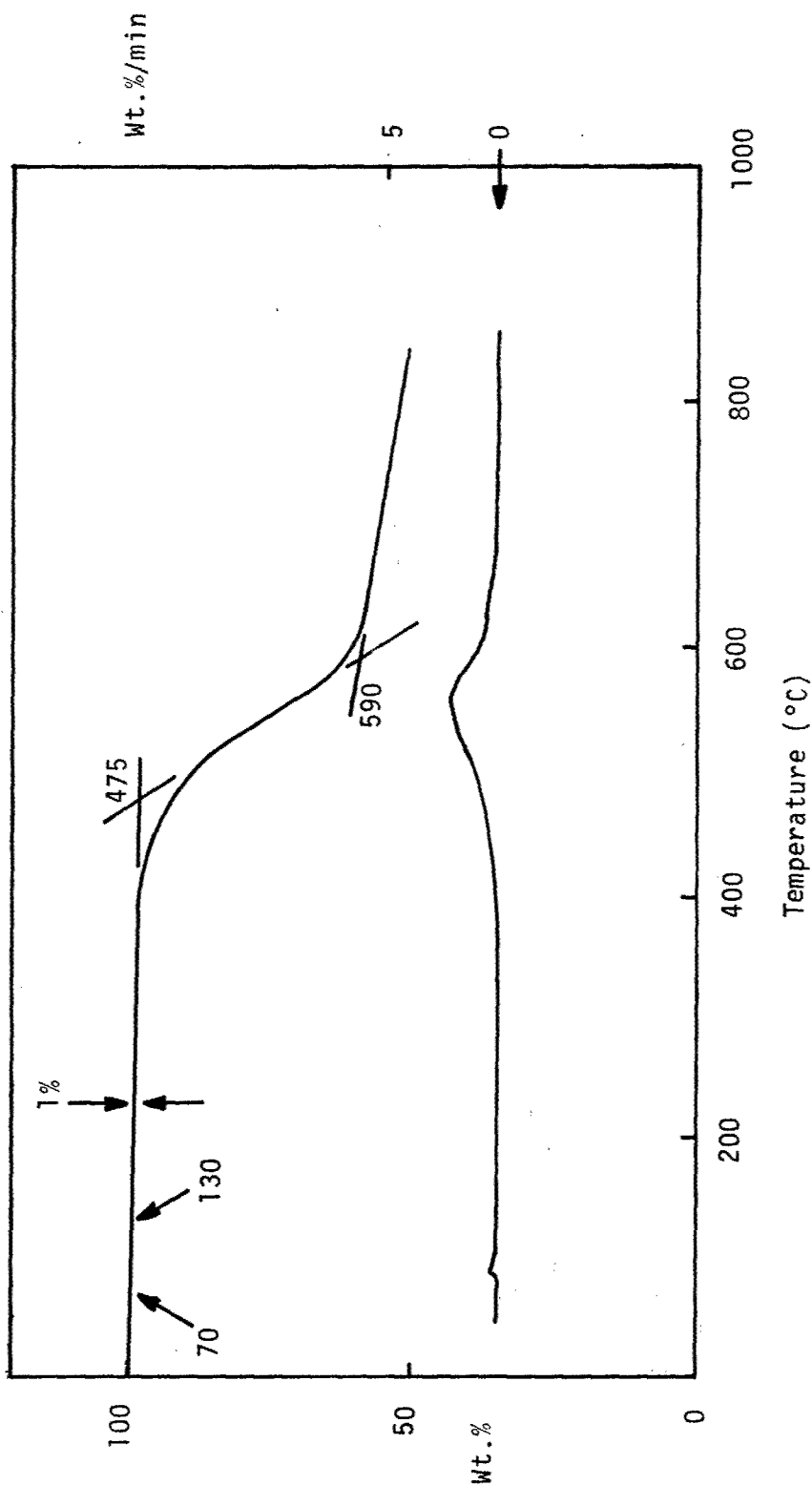


Figure 50. Programmed TGA of ATS Dimer (F2) Under Helium

Heating rate 5°C/min  
Sample size 13.50 mg

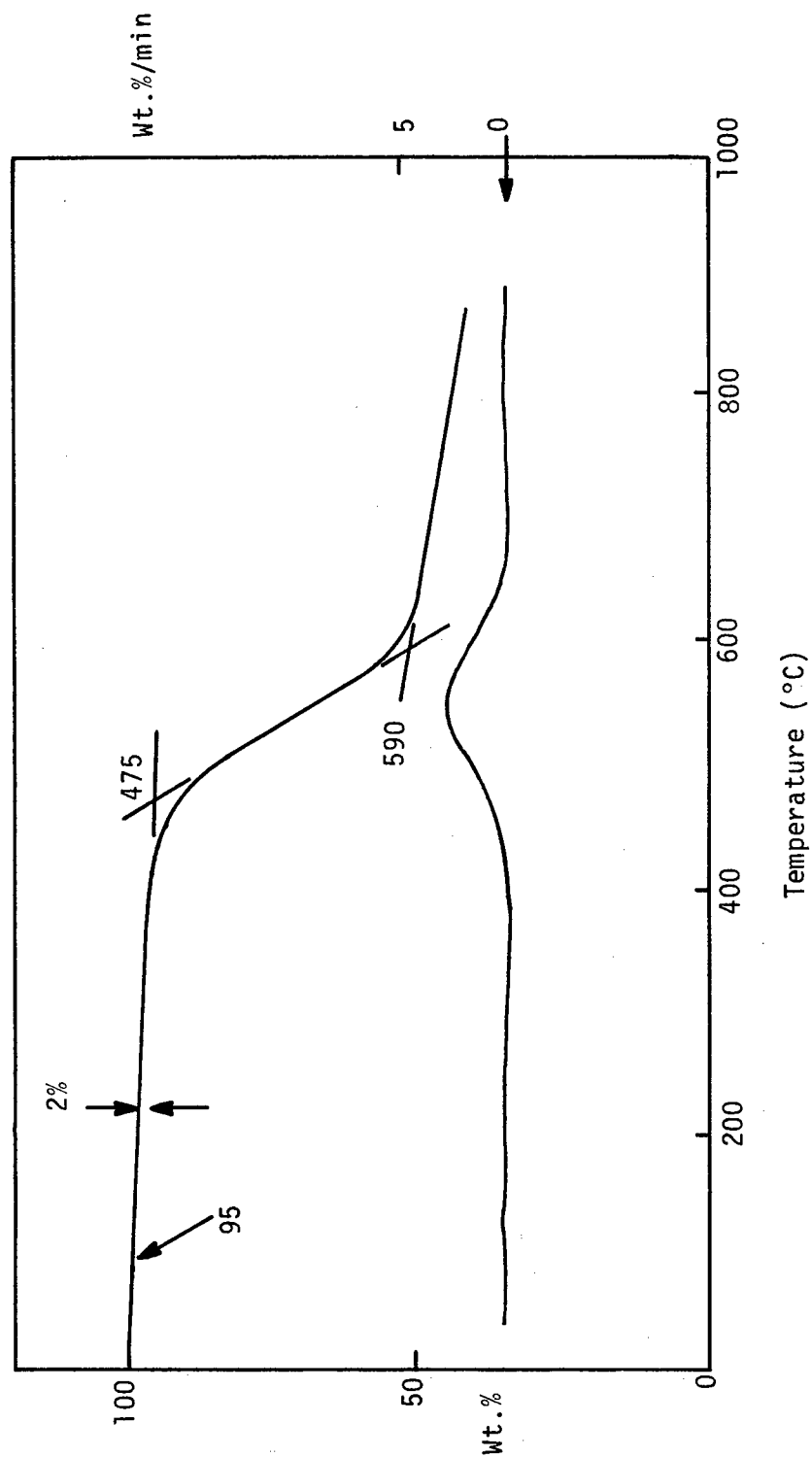


Figure 51. Programmed TGA of ATS Trimer (F3) Under Helium

Heating rate 5°C/min  
Sample size 10.65 mg

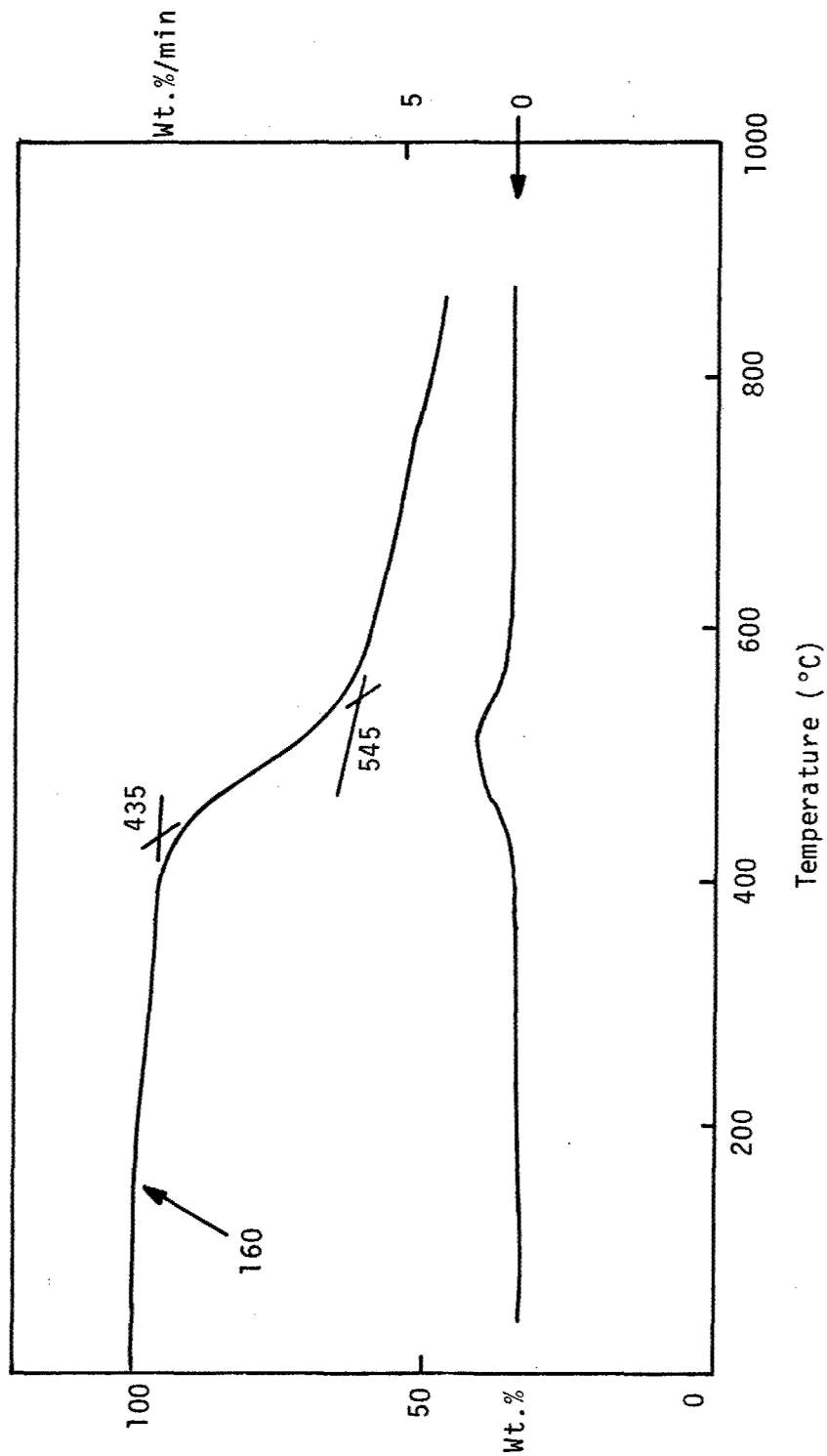


Figure 52. Programmed TGA of F4 Under Helium

Heating rate 5°C/min  
Sample size 11.10 mg

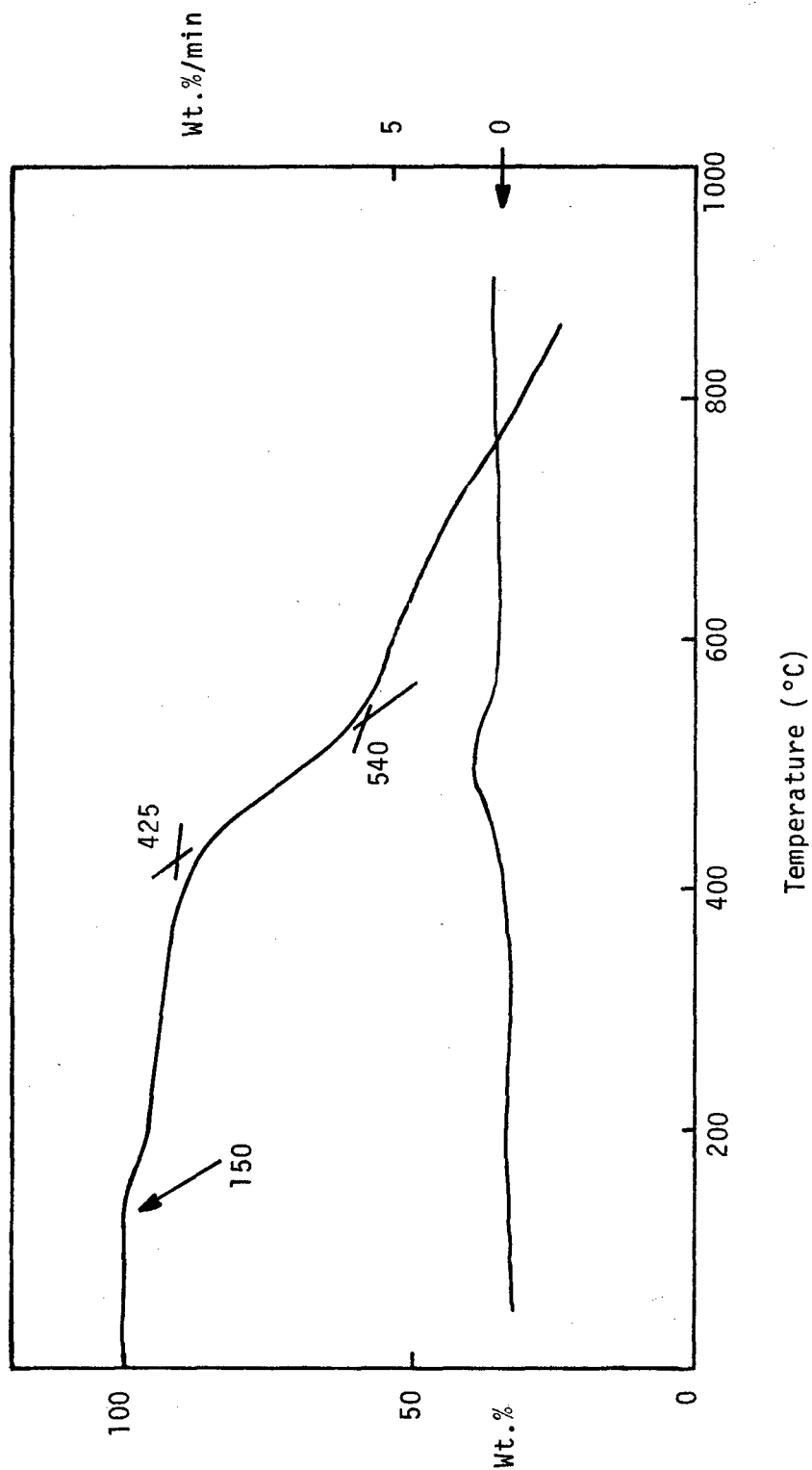


Figure 53. Programmed TGA of F5 Under Helium

Heating rate 5°C/min  
Sample size 15.40 mg

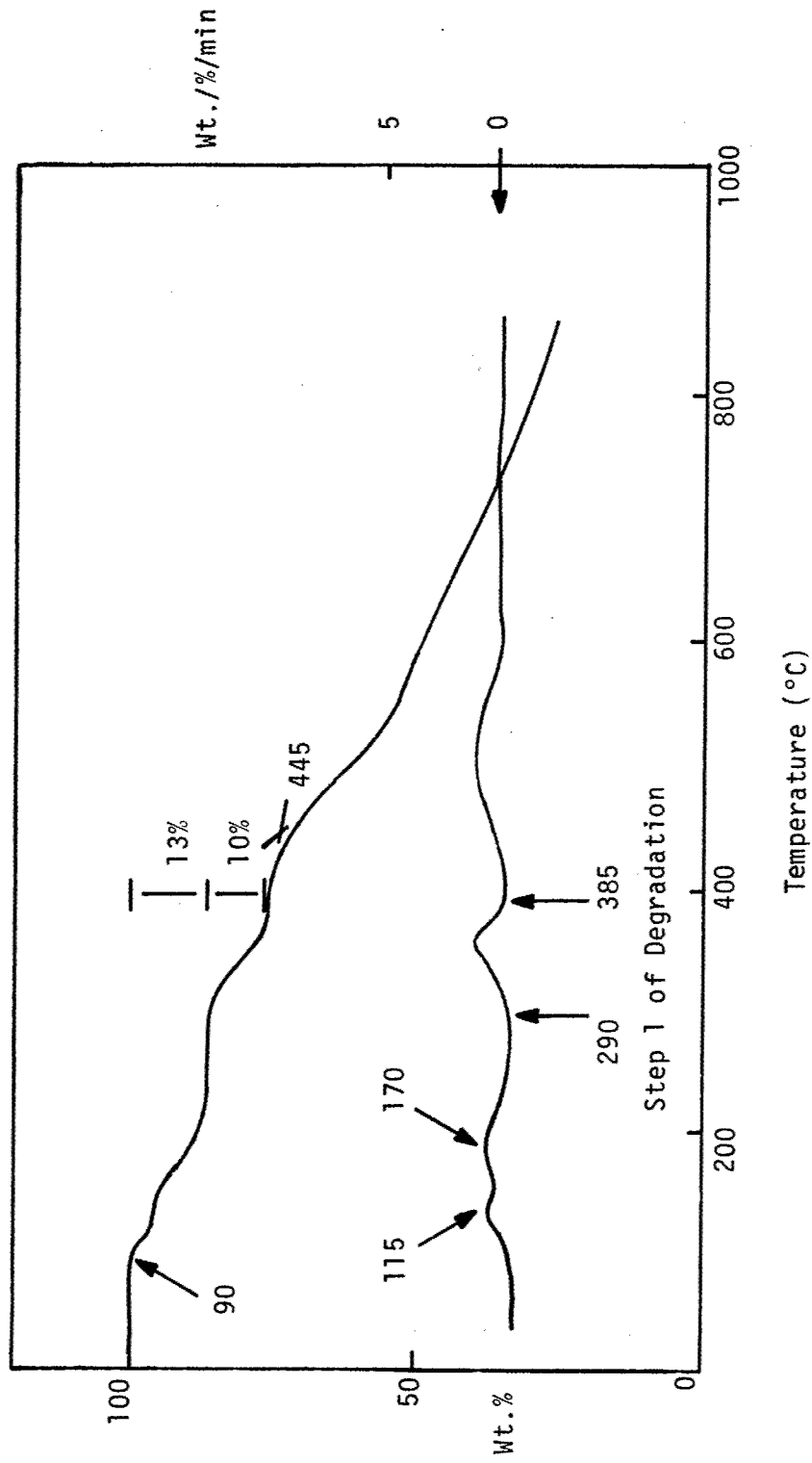


Figure 54. Programmed TGA of VAA (F7) Under Helium

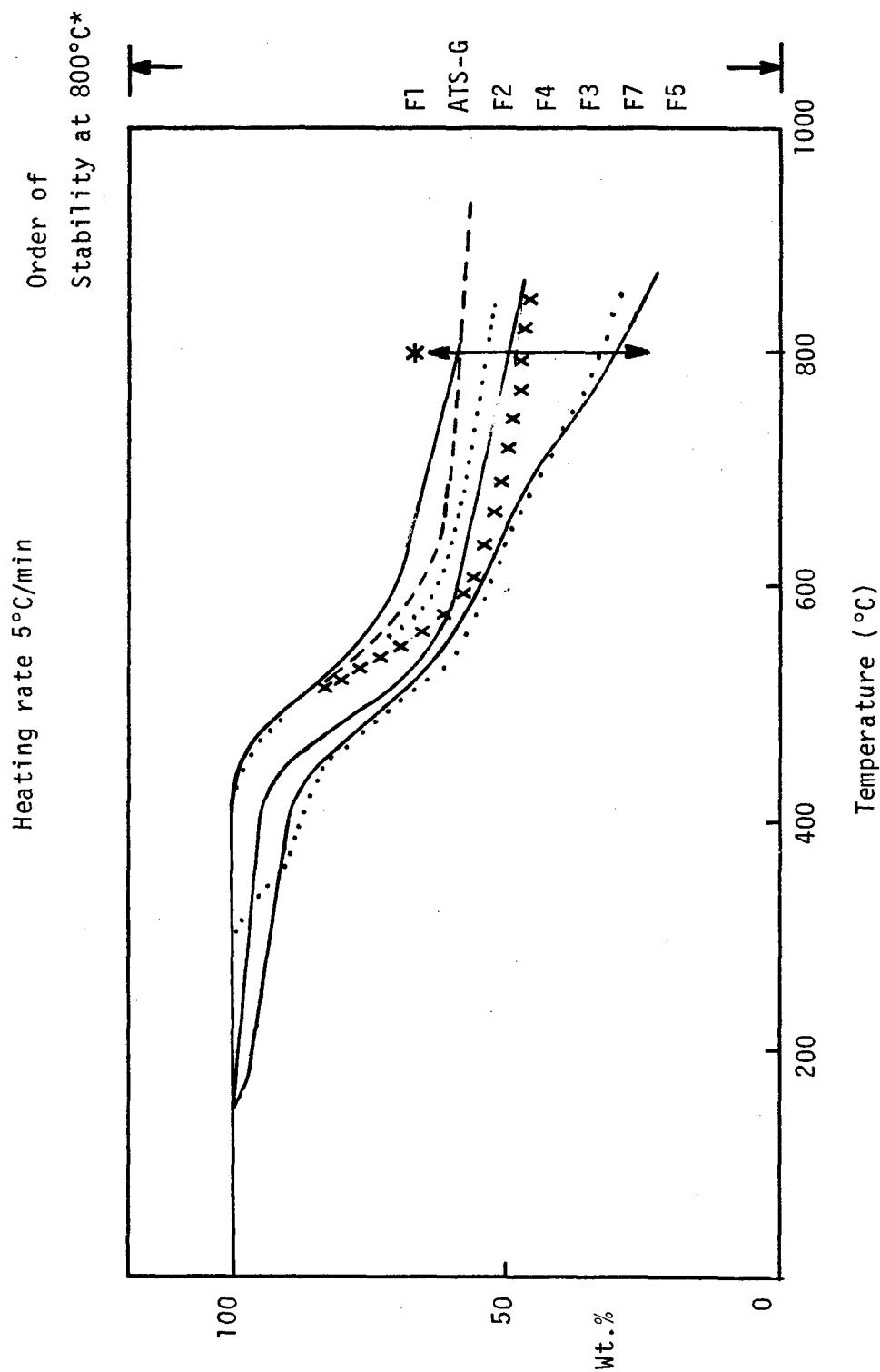


Figure 55. A Comparison Between Solvent Compensated TGA Curves for ATS-G and its Components

REFERENCES

1. I. J. Goldfarb, C. Y-C. Lee and C. C. Kuo, Organic Coatings and Applied Polymer Science Proceedings, 47, 600 (1982)
2. I. J. Goldfarb and W. T. K. Stevenson, "Thermal Degradation of ATS-G", AFWAL - TR (In Print)
3. M. Unroe, M.S. Thesis, Wright State University, (1982)
4. J. M. Pickard, S. C. Chatteraj, G. A. Loughran and M. T. Ryan, Macromolecules, 13, 1289 (1980)
5. H. L. Friedman, J. Polym. Sci., C, 6, 183 (1965)
6. W. W. Adams and I. J. Goldfarb, AFWAL - TR - 81 - 4177
7. K. R. Fisch, AFML - TR - 74 - 163
8. J. J. Harrison and C. M. Selwitz, AFML - TR - 79 - 4183